

Measurement of Atmospheric Dry Deposition at Emerald Lake  
in Sequoia National Park

Final Report

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## ABSTRACT

The primary objective of this study was to assess atmospheric dry deposition of major anions and cations to trees at the Emerald Lake area of the Sequoia National Park. The field work was performed between July 15, 1987 and September 10, 1987, utilizing three time periods without wet precipitation for dry deposition determinations. Materials deposited on Teflon film coated and non-coated branches of two native coniferous species, lodgepole pine (Pinus concorta) and western white pine (P. monticola), as well as potted seedlings of Coulter pine (P. coulteri) were rinsed from the foliage with deionized-distilled water. Atmospheric ions deposited to two surrogate surfaces (nylon and paper filters) were extracted from the filters in deionized-distilled water. Acidity, conductivity, and concentrations of nitrate, sulfate, phosphate, chloride, fluoride, ammonium and metallic cations were determined in foliage rinses and filter extracts. Deposition fluxes of the studied ions to tree foliage and surrogate surfaces as well as conductivity of needle rinses and filter extracts have been determined.

Deposition fluxes of the majority of the measured ions to the lodgepole and western white pines were similar during all three exposure periods. However, deposition fluxes of chloride and ammonium were the highest during the second period of exposures (August 4-12, 1987). No significant differences were found between deposition rates to Teflon-coated branches and to non-Teflon branches. This indicates that for these two conifers, no significant extraction of ions during the washing procedures or uptake of ions deposited on needle surfaces by the needle interior took place. Highest deposition fluxes were determined for nitrate, ammonium, calcium and sodium. Deposition fluxes of sulfate were several times lower than deposition fluxes of nitrate.

For Coulter pines deposition rates of sulfate and phosphate were significantly higher for non-Teflon coated branches than for Teflon coated branches. This indicates that a significant extraction of ions from the needle interior during the washing procedures was taking place. Rinsing of branches enclosed in the clean-air chamber provided a mechanism to estimate amounts of ions being extracted from the needles (both Teflon and non-Teflon coated). After subtracting the extractable ions, the net dry

deposition fluxes to the Teflon-coated branches and to the non-Teflon coated branches became similar, and in the range of values determined for the native pines. Highest values of deposition fluxes were found for nitrate, sulfate, ammonium, calcium and sodium.

Deposition fluxes of some ions (especially chloride, ammonium, sodium and hydrogen) to the nylon and paper filters were quite different from the fluxes determined for the pine branches. For the nylon filters high deposition fluxes of nitrate, chloride, calcium and sodium were determined. Nitrate, ammonium, calcium and sodium deposition fluxes were the highest for the paper filters. No deposition fluxes of phosphate to these filters was found.

Comparison of nitrate:sulfate and ammonium:sulfate ratios revealed that the fluxes of nitrogen compounds to the native coniferous species at Emerald Lake are of a greater importance than the sulfur compounds fluxes. This finding is similar to the ratio of these ions determined for the chaparral species in the mountains of the South Coast Air Basin, California, during the summer of 1985.

Balancing deposition of anions and cations to different surfaces indicates a deficit of anions. This suggests that anions not measured during this study (organic anions and carbonate) may play a more important role than previously thought in dry deposition.

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## SUMMARY AND CONCLUSIONS

Very little is known about atmospheric dry deposition to native vegetation in general, and especially in the western United States. Dry deposition to plant communities in the Sierra Nevada is of a special importance because of the small amounts of wet deposition during the vegetative season, and the scarcity of nutrients in the predominately granite soils. Information on the levels of atmospheric dry deposition to forest vegetation is of great importance because of its potential influence on plant health, on biomass production, on nutrient balance, on nutrient cycling, and on fuel accumulation rates.

Atmospheric dry deposition at the Emerald Lake site (altitude of about 2740 m) was studied between July 15, 1987 and September 10, 1987. Fluxes of atmospheric dry deposition to branches were investigated for native conifers, lodgepole pine (Pinus concorta) and western white pine (P. monticola), potted seedlings of Coulter pine (P. coulteri), and nylon and Whatman paper filters as surrogate leaf surfaces.

Rinsing of branches with deionized-distilled water was used to remove the materials deposited on plant surfaces. Teflon coating of branches provided a means of reducing experimental error caused by movement of ions from the leaf surface to the needle interior during the exposure periods, and by leakage of nutrients from the inside of needles during the rinsing procedures. For the Coulter pine seedlings, an additional assessment of nutrient leakage from the needle interior during the rinsing procedures was made. This assessment involved enclosure of the pine seedlings in a particle-free chamber, with Teflon coated and non-Teflon coated branches of these seedlings rinsed with deionized-distilled water every two weeks. Atmospheric ions deposited on the nylon and paper filters were extracted with deionized-distilled water. Solution acidity was measured with a pH electrode, and conductivity with a conductivity meter. Concentrations of nitrate, sulfate, phosphate, chloride and fluoride in the solutions were determined by ion chromatography, concentrations of ammonium by colorimetry, and metallic ions by an inductively coupled plasma (ICP) method.

No significant movement of nutrients between needle interior and surface for lodgepole and western white pine was found. For these species

deposition fluxes of the studied ions were in the ranges shown in Table 1. Average deposition fluxes of anions and cations to the lodgepole pine for the entire study were several times lower than dry deposition values determined during the corresponding period of 1986 for Ceanothus crassifolius at Tanbark Flat of the San Gabriel Mountains, South Coast Air Basin (Figure 1). Nitrate and ammonium deposition to the native pine branches at Emerald Lake were higher than deposition of sulfate, indicating a greater importance of nitrogen than sulfur compounds in this area.

Coulter pine exhibited tendency towards higher deposition fluxes for the non-Teflon coated branches of potted seedlings compared with the coated branches. This difference may be an indication of nutrient leakage from the needle interior during the rinsing procedures. However, a possibility of lower adsorption of the particles to the Teflon coated branches during the exposure periods should also be considered. After subtracting the results obtained for the seedlings enclosed in the particle-free chamber, the results for the coated and non-coated branches were similar. These results were in the ranges shown in Table 1. For most of the studied ions the deposition fluxes were in the range of the values determined for the lodgepole and western white pines. Deposition fluxes of sulfate, phosphate, calcium and magnesium to Coulter pine were significantly higher than to the two native pines, probably due to differences in the deposition velocities of these ions caused by dissimilarities in the roughness of needle surfaces.

Deposition fluxes of nitrate or sulfate to the nylon and paper surrogate surfaces were generally in the same range as the values for the conifers (Table 1). However, deposition fluxes of other ions to the nylon and paper filters were different than deposition fluxes to the conifers. No phosphate ions were deposited to both of the surrogate surfaces. Deposition fluxes of chloride to nylon filters were much higher than to any other surfaces. Deposition fluxes of ammonium were very high for the paper filters, exceeding the values obtained for all other surfaces. However, deposition fluxes of ammonium were very low for the nylon filters.



Table 1. Ranges in deposition fluxes of ions deposited to pine needles and surrogate surfaces.

Ion	Lodgepole and Western White Pines	Coulter Pine	Nylon Filter	Paper Filter
(μEq m <sup>-2</sup> h <sup>-1</sup> )				
NO <sub>3</sub> <sup>-</sup>	0.360-0.597	0.448-0.699	0.542-0.702	0.407-1.052
SO <sub>4</sub> <sup>2-</sup>	0.044-0.121	0.158-0.387	0-0.163	0.100-0.196
PO <sub>4</sub> <sup>3-</sup>	0-0.067	0.091-0.180	≈0	≈0
Cl <sup>-</sup>	0.038-0.383	0.091-0.255	1.332-2.593	0.248-0.390
F <sup>-</sup>	0.014-0.066	0.010-0.106	≈0	0.002-0.024
NH <sub>4</sub> <sup>+</sup>	0.163-0.656	0.101-0.305	0-0.147	1.053-1.826
Ca <sup>2+</sup>	0.300-0.456	0.525-1.103	0.541-1.128	0.450-0.543
Mg <sup>2+</sup>	0.109-0.216	0.200-0.275	0.022-0.090	0.011-0.040
Na <sup>+</sup>	0.174-0.564	0.295-0.912	0.922-1.586	0.966-1.926
Zn <sup>2+</sup>	0-0.010	0-0.017	0.022-0.045	0.013-0.026
Fe <sup>3+</sup>	≈0	0.065-0.117	0.064-0.108	0.035-0.057
Mn <sup>2+</sup>	≈0	0.04-0.009	0.006-0.080	0.002-0.007
Pb <sup>2+</sup>	≈0	≈0	0.032-0.080	0.033-0.067
H <sup>+</sup>	0-0.256	0-0.113	1.084-2.617	0-0.249

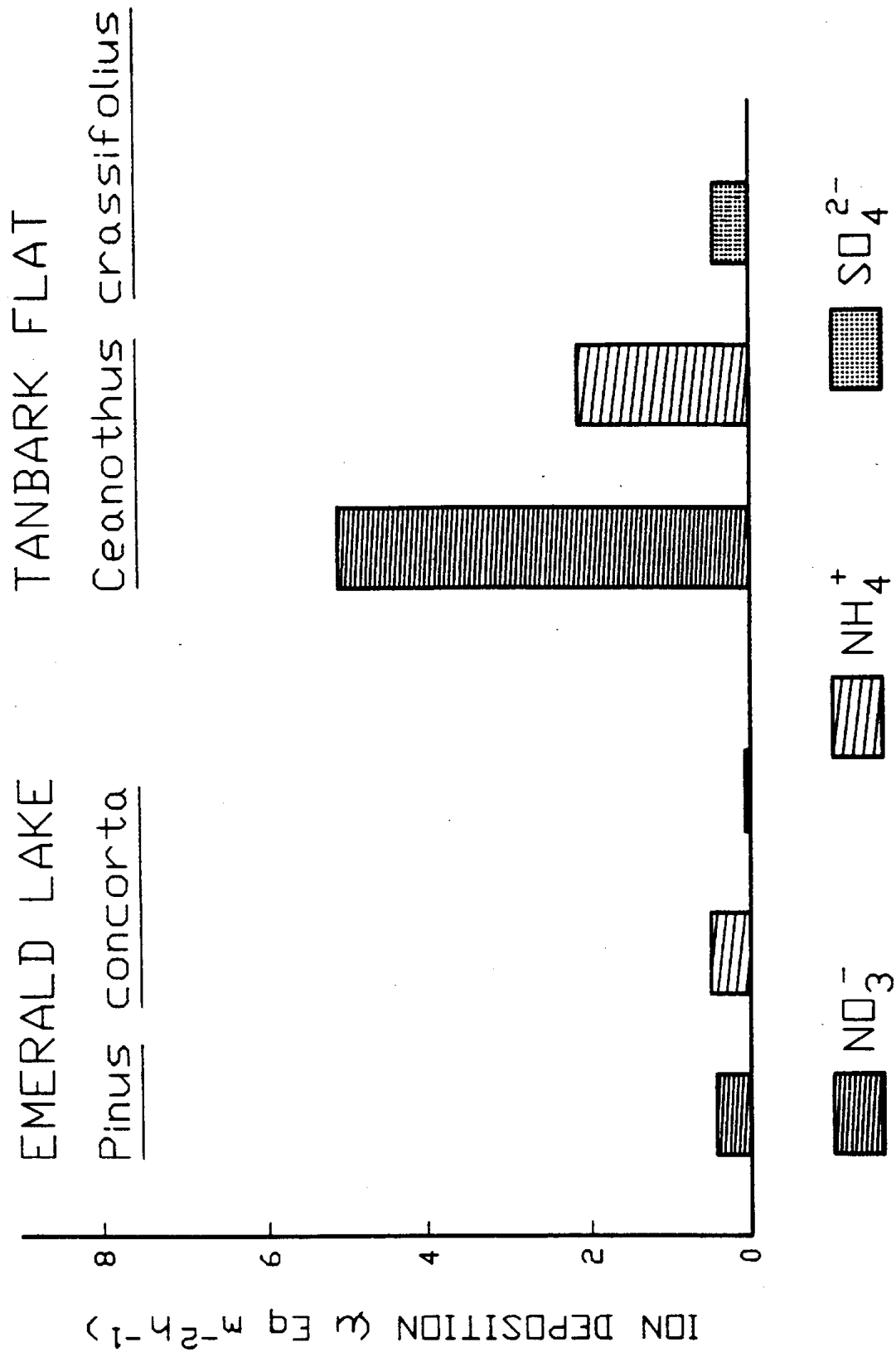


Figure 1. Comparison of dry deposition fluxes of nitrate, ammonium and sulfate ions to native trees at Emerald Lake (Sequoia National Park) and Tanbark Flat (San Gabriel Mountains)-summers of 1988 and 1986, respectively.

Comparison of the ratios of nitrate:sulfate and ammonium:sulfate deposition fluxes to the native conifers at Emerald Lake revealed that the nitrogen compounds are of much higher importance than the sulfur compounds, as reported previously for chaparral species in the South Coast Air Basin (Figure 2). Especially interesting is a high proportion of ammonium ion in dry deposition to native pines at Emerald Lake, which may be an indication of ammonia and ammonium transport from the San Joaquin Valley (Figure 3). Increased deposition of nitrogen compounds to the forest ecosystem together with increased concentrations of ozone may have significant effects on forests in the western part of the Sierra Nevada Mountains.

The conclusions from the study are as follows:

a. Deposition fluxes of nitrate, ammonium and sulfate to lodgepole and western white pine at Emerald Lake were several times lower than deposition fluxes to Ceanothus crassifolius at the highly polluted site of Tanbark Flat in the San Gabriel Mountains, South Coast Air Basin.

b. Nitrate and ammonium fluxes to the native pines were at the same level, and several times greater than the sulfate fluxes. This finding indicates an importance of nitrogen compounds in the western Sierra Nevada probably caused by movement of atmospheric particulate nitrate, nitric acid, ammonium and ammonia from the San Joaquin Valley.

c. Deposition fluxes of nitrate, sulfate, zinc, iron, manganese and lead were in the same ranges for both plant and surrogate surfaces; but deposition fluxes of phosphate, chloride, fluoride, ammonium, and sodium differed greatly among the studied surfaces.

d. The results from Emerald Lake once again confirm that in the western United States, contrary to the eastern part of the country, atmospheric deposition of nitrate is more important than deposition of sulfate.

e. Balancing deposition of anions and cations to different surfaces indicates a deficit of anions. This suggests that anions not measured during this study (organic anions and carbonate) may play a more important role than previously thought in dry deposition.

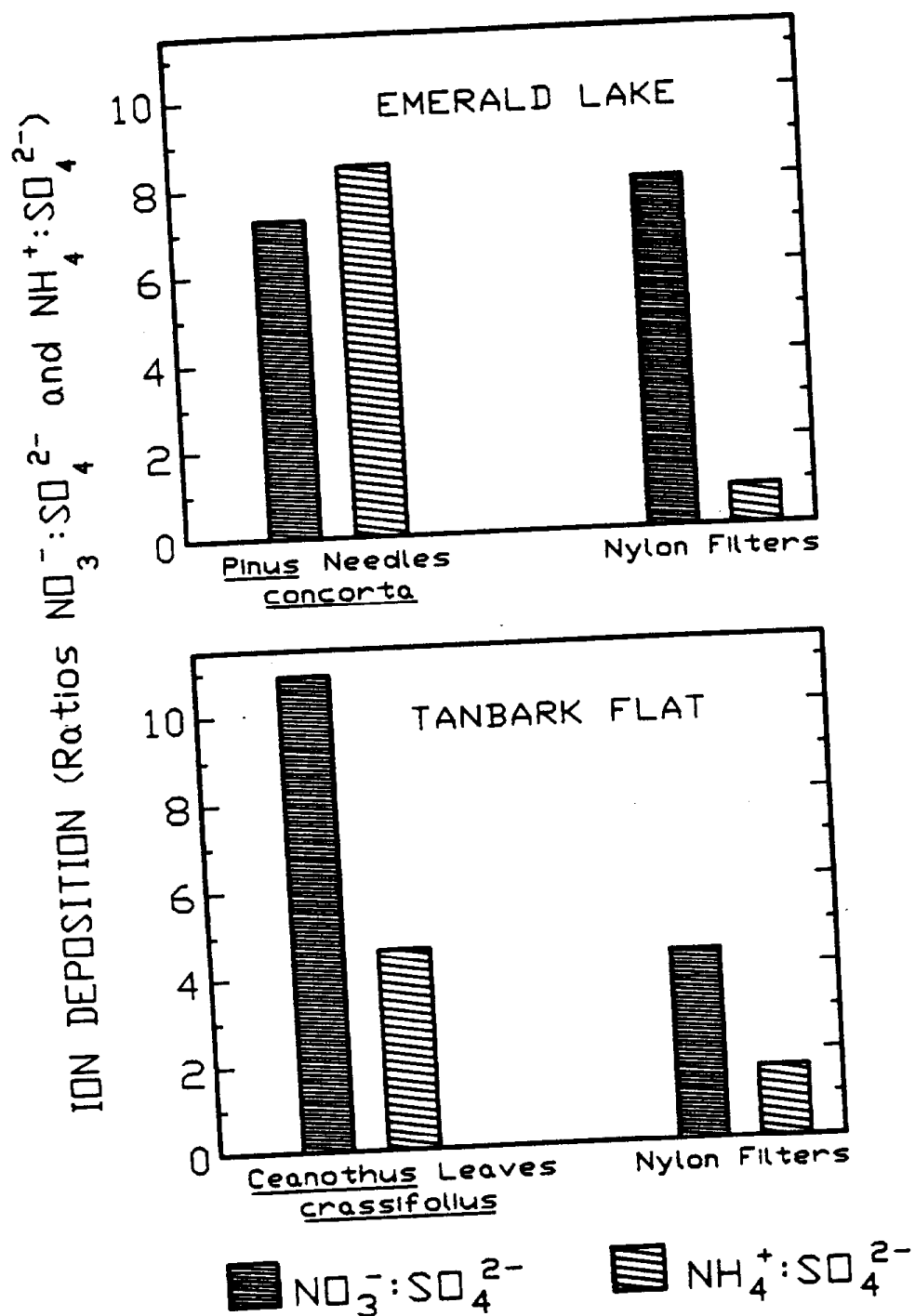


Figure 2.  $\text{NO}_3^-:\text{SO}_4^{2-}$  and  $\text{NH}_4^+:\text{SO}_4^{2-}$  ratios in atmospheric dry deposition to native trees at Emerald Lake (Sequoia National Park) and Tanbark Flat (San Gabriel Mountains)-summers of 1988 and 1986, respectively.

# Pinus concorta Needles

(NO TEFLON)

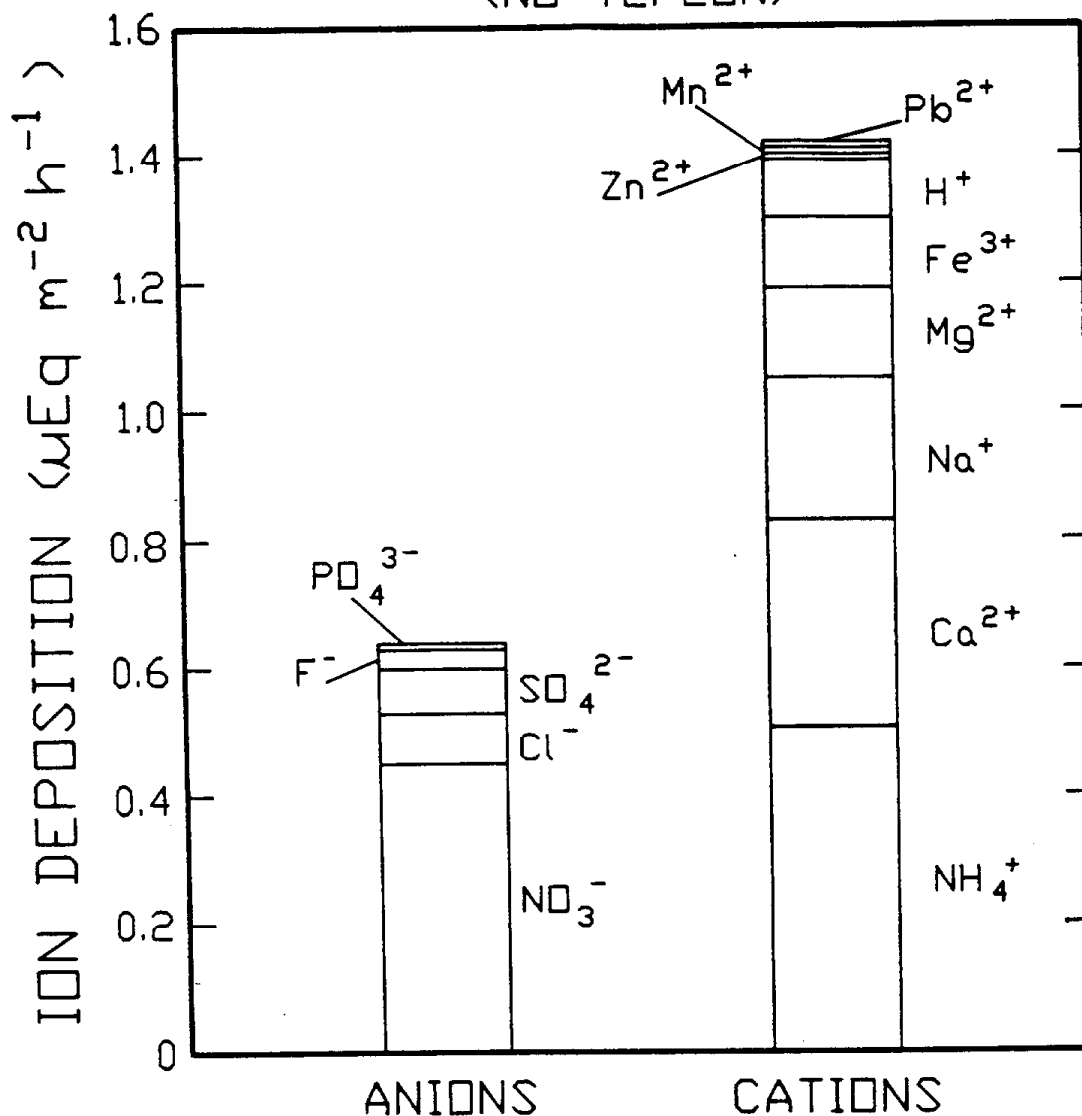


Figure 3. Ionic deposition to lodgepole pine (Pinus concorta) at Emerald Lake (Sequoia National Park)-averages for the entire study.

f. Both coating of plant foliage with a Teflon film, to prevent ion movements between leaf surface and leaf interior, and calculation of the deposition fluxes in the clean-air chambers, to estimate ion extraction from the needle interior during the rinsing procedures, improve the reliability of estimations of atmospheric dry deposition to plant surfaces.

## RECOMMENDATIONS

1. More studies on dry deposition to native plant species are needed for the western United States - the present knowledge of the subject does not allow for a comparison of results from Emerald Lake with results from other areas with higher pollution exposure.

2. More studies aimed at linking dry deposition to plants with nutrient cycling in forest ecosystems are needed to assess the importance of this nutritional input for development of forest trees.

3. Further development of dry deposition measurement techniques is needed - at present many problems related to the movement of ions between the surface and interior of the foliage, as well as the effect of wind movement, surface roughness, air and surface moisture, etc. are not fully understood. Testing of other methods preventing ion movement between leaf surface and leaf interior is recommended. Such tests should be evaluated by chemical analysis and scanning electron microscopy.

4. Calculation of deposition velocities of the studied ions is recommended. Such calculations may be possible when data on atmospheric concentrations of the studied ions are available.

5. Measurements of deposition fluxes of organic anions and carbonate to plant surfaces are needed to balance anion and cation depositions to plant canopies.





## I. INTRODUCTION

Atmospheric dry deposition is an important process of ionic transfer in many ecosystems, especially those with a long dry season. Even in the humid forests of the southeastern United States, 19 to 64% of the total annual deposition of ions such as Ca, Na, K, and Mg, and up to 89% of the deposition of P were derived through dryfall (Waring and Schlesinger, 1985). Dry deposition may be even more important in the Sierra Nevada, where it may be a substantial component of total atmospheric deposition (Stohlgren and Parsons, 1987).

Atmospheric dry deposition to plant canopies has been studied in parts of Europe and eastern United States, revealing that sulfur compounds were the main cause of acidity (Hicks, et al., 1982; Lindberg and Lovett, 1983, 1985; Lindberg et al., 1984, 1986; Lovett and Lindberg, 1984; Gravenhorst and Hofken, 1982; Hofken and Gravenhorst, 1982; Gravenhorst et al., 1983). Dry deposition to chaparral vegetation in southern California has also been investigated (Schlesinger et al., 1982; John et al., 1984; Ondo et al., 1984; Riggan et al., 1985; Bytnerowicz et al., 1987a). Studies in the San Gabriel Mountains of the South Coast Air Basin during the summer of 1985 have shown that large amounts of nitrate and ammonium are deposited as dryfall to the chaparral plant canopies. Deposition of nitrogen compounds to vegetation canopies in this area is much more important than deposition of sulfur compounds. This situation is caused by high concentrations of  $\text{NO}_x$ , particulate nitrate, nitric acid vapors and particulate ammonium in the air of that area (Bytnerowicz et al., 1987b).

Very little is known about dry deposition to native vegetation in other parts of the western United States, including the Sierra Nevada. A pilot study in the Eastern Brook Lake area (a subalpine environment of the eastern Sierra Nevada) showed that atmospheric deposition to branches of potted ponderosa and Coulter pine seedlings was less acidic, and had significantly lower concentrations of nitrate than dry deposition to branches of the same species in the San Gabriel Mountains (Bytnerowicz et al., unpublished). Information on the levels of dry deposition to forest vegetation in other parts of the Sierra Nevada is of great importance because of its potential influence on plant health, biomass production, nutrient balance, nutrient cycling and fuel accumulation rates.

The primary objective of the study was to assess dry deposition of major ions to trees at the Emerald Lake area of the Sequoia National Park. A secondary objective was to try to balance anions and cations in the materials deposited to the plant and surrogate surfaces. Another secondary objective was to improve the accuracy of foliage rinsing techniques used the assessment of dry deposition to plants through the Teflon coating of branches, and the enclosure of control plants in a clean air chamber.

To accomplish these objectives, we measured atmospheric dry deposition to the native conifers and potted pine seedlings, as well as to two different surrogate surfaces. Leakage of nutrients from the foliage during rinsing procedures and transport of ions between the interior of the foliage during the exposure periods have been considered as important factors affecting a precision of dry deposition estimations using foliage rinsing procedures. In the reported study we attempt to evaluate the importance of these factors.

## II. METHODS

### A. Selection of the Site

The site for dry deposition measurements was selected at the end of June during a field trip attended by participants from the Sequoia National Park, California Air Resources Board, U.C. Davis and U.C. Riverside. The site was located at about 2740 m elevation, on a granite slope open to the west about 200 m south of the Research Camp at Emerald Lake.

### B. Dry Deposition Collection

Dry deposition measurements started on July 15, 1987 and lasted until September 10, 1987. Three 2-week long periods of dry deposition exposures were planned; however, after consulting with the California Air Resources Board staff, an additional fourth exposure was added to the study. Rain occurred several times during the study. As a result, dry deposition was determined only for three periods of exposure, July 15-29; August 4-12, and September 3-10, 1987. For the August and September exposures the time period was less than 2 weeks. Dry deposition to native conifers, potted conifer, and two surrogate surfaces were investigated during the study.

#### Native Conifer Species

Native conifer species in the Emerald Lake area were used for the study and consisted of four lodgepole pine (Pinus concorta) trees and four western white pine (P. monticola) trees. Two branches on the western side of each tree were selected. The chosen branches were 5 to 10 cm long. Each branch was thoroughly washed with deionized - distilled water dispersed from plastic spray bottles. When dry, one of the branches on each tree was sprayed with Teflon (TFE lubricant permanent film 6078, Crown Industrial Products Co., Hebron, Illinois). The branches were covered with Teflon film to prevent movement of ions between the surface and interior of the foliage during exposure periods, and to prevent the leaching of ions from the leaf interior during the rinsing procedures. The other washed branch on each tree was not coated with Teflon. At the end of each exposure period the branches were rinsed with about 80 mL of deionized - distilled water. The rinsing solutions were collected in 130 mL plastic bottles and immediately placed in cool-boxes filled with dry

ice. The samples were kept frozen ( $-18^{\circ}\text{C}$ ) prior to analysis. At the end of the study the branches were cut, and surface areas of the needles and twigs were calculated.

#### Potted Conifers

Four 2-year old seedlings of Coulter pine (Pinus coulteri) in pots were placed in the vicinity of the native pines used for the study. As for the native pines, two branches on each tree were selected for the dry deposition measurements. After washing with deionized - distilled water, one of the branches was coated with a Teflon film, while the second branch was left uncoated. Four Coulter pine seedlings with similar appearance were placed in the aerosol-free chamber. The air was drawn into this chamber through a HP-200 high performance air filter, (Farr Company) providing 99.7% efficiency for 2 micron size particles, and through activated charcoal. The aerosol-free chamber was placed inside a greenhouse with charcoal-filtered air located at a field site in the Agricultural Operations area at U.C. Riverside. Rinsing of the needles enclosed in the particle-free chamber was used to determine the amount of material extracted from the needle interior during the washing procedures. At the end of each exposure period the Coulter pine branches were rinsed according to the procedures described for the native conifers. At the end of the study the branches were cut, and their surface areas determined.

#### Surrogate Surfaces

1.0 micrometer pore-size nylon filters, 47 mm in diameter (Nylasorb, Membrana Products, Pleasanton, CA), and Whatman No. 41 paper filters, 47 mm in diameter, were held in nylon double rings at a height about 50 cm above the ground. Both surrogate surfaces were exposed in a horizontal position. The filters were changed at the same time the conifer branches were rinsed. The exposed filters were placed in 60 mm diameter Petri dishes and were additionally enclosed in tightly closed plastic bags. Immediately after the collection the filters were placed in cool-boxes filled with dry ice. Prior to extraction the filters were kept at  $-18^{\circ}\text{C}$ .

### C. Chemical Analysis

The foliage rinses were thawed and brought up to 100 mL volume. Nylon and paper filters were placed in 250 mL Erlenmayer flasks with 100 mL of deionized-distilled water and extracted for 15 min on an automatic laboratory wrist shaker. The extracts were filtered through Schleicher & Schuell Co. No. 591A paper filters. The pH of foliage rinses and filter extracts was measured with a Ross electrode and Orion Ionalyzer; conductivity was measured with a Markson conductivity meter. All measurements were done at the University of California, Riverside.

20 mL of each sample was transferred into 60 mL plastic bottles and acidified with 0.2 mL of Ultrex nitric acid (J.T. Baker Chemical Company). These samples were sent to the Biomedical and Environmental Sciences Laboratory, U.C.L.A., for determination of metallic cations with an inductively coupled plasma (ICP) method. Due to a high detection limit of the ICP method to potassium, the results obtained for this element were not reliable. Therefore these results were not included in this report. The remainder of the samples were sent to Global Geochemistry Corporation (Canoga Park, CA) for the analysis of nitrate, sulfate, phosphate, chloride and fluoride (ion chromatography) and ammonium (colorimetry).

### D. Calculation of the Results and Statistical Analysis

Fluxes of ions to plant foliage and to surrogate surfaces are presented as microequivalents per square meter per hour. The results are presented as means and standard deviations for four replicate measurements. Analysis of variance, Duncan's multiple-range test, and multiple correlation analyses were used for the statistical evaluation of the data (Steel and Torrie, 1980).



### III. RESULTS

#### A. Dry Deposition to Native Conifers

Deposition fluxes of ions to branches and conductivity of branch rinses for the Teflon-coated foliage of lodgepole pine (Pinus concorta) are presented in Table 2. Deposition fluxes of nitrate, sulfate, fluoride, calcium, magnesium, sodium, zinc, iron, manganese and hydrogen were similar for all of the three exposure periods. Deposition fluxes of chloride and ammonium differed between the particular exposure periods, reaching the highest values during the second period. Deposition fluxes of phosphate and lead were below detection limits for all the periods of exposure. Conductivity of leaf rinses was the highest for the second period of exposures. The deposition fluxes of ions to branches and conductivity of branch rinses for the non-Teflon coated foliage of lodgepole pine are presented in Table 3. As for the branches coated with Teflon, deposition fluxes of nitrate, sulfate, phosphate, calcium, magnesium, sodium, zinc, iron, manganese, and hydrogen were similar for all of the three exposure periods. Deposition fluxes of chloride and ammonium were the highest during the second period of exposure. There were no significant differences between deposition fluxes to the Teflon-coated and non-Teflon coated branches, suggesting that there was no significant uptake of ions deposited on the needle surface by the needle interior nor was there leaching of ions from the foliage during the rinsing procedures.

Deposition fluxes of ions to branches and conductivity of branch rinses for the Teflon-coated foliage of western white pine (Pinus monticola) are shown in Table 4. Deposition fluxes of nitrate, sulfate, phosphate, fluoride, calcium, magnesium, sodium, zinc, iron, manganese, and hydrogen were at the same levels during all three exposure periods. However, deposition fluxes of chloride, ammonium, and conductivity of branch rinses were the highest during the second exposure period. For the branches not coated with Teflon (Table 5), deposition fluxes of the majority of ions as well as conductivity values were similar during all the exposure periods. Deposition fluxes of hydrogen were the highest during the third period of the exposures. As for lodgepole pine, deposition fluxes to the Teflon-coated and non-coated foliage of western

Table 2. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Lodgepole Pine (*Pinus contorta*) - Branches Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.366 \pm 0.142$	$0.519 \pm 0.167$	$0.378 \pm 0.091$
$\text{SO}_4^{2-}$	$0.059 \pm 0.027$	$0.093 \pm 0.023$	$0.064 \pm 0.018$
$\text{PO}_4^{3-}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{Cl}^-$	$0.067 \pm 0.015$ ab	$0.096 \pm 0.048$ a	$0.025 \pm 0.014$ b
$\text{F}^-$	$0.023 \pm 0.003$	$0.041 \pm 0.008$	$0.022 \pm 0.009$
$\text{NH}_4^+$	$0.243 \pm 0.075$ b	$0.609 \pm 0.204$ a	$0.493 \pm 0.146$ ab
$\text{Ca}^{2+}$	$0.300 \pm 0.143$	$0.439 \pm 0.087$	$0.328 \pm 0.059$
$\text{Mg}^{2+}$	$0.139 \pm 0.099$	$0.143 \pm 0.025$	$0.114 \pm 0.026$
$\text{Na}^+$	$0.319 \pm 0.175$	$0.342 \pm 0.199$	$0.204 \pm 0.023$
$\text{Zn}^{2+}$	$0.004 \pm 0.002$	$0.007 \pm 0.003$	$0.000 \pm 0.000$
$\text{Fe}^{3+}$	$0.102 \pm 0.096$	$0.095 \pm 0.031$	$0.099 \pm 0.024$
$\text{Mn}^{2+}$	$0.005 \pm 0.002$	$0.008 \pm 0.001$	$0.007 \pm 0.001$
$\text{Pb}^{2+}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{H}^+$	$0.055 \pm 0.053$	$0.107 \pm 0.031$	$0.120 \pm 0.293$
Conductivity	$0.963 \pm 0.372$ ab	$1.805 \pm 0.660$ a	$0.815 \pm 0.771$ b
Total anions	0.515	0.749	0.489
Total cations	1.167	1.750	1.365

<sup>a</sup> Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.



Table 3. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Lodgepole Pine (Pinus concorta) - Branches Not Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.483 \pm 0.219$	$0.484 \pm 0.138$	$0.360 \pm 0.170$
$\text{SO}_4^{2-}$	$0.090 \pm 0.043$	$0.062 \pm 0.006$	$0.044 \pm 0.034$
$\text{PO}_4^{3-}$	$0.028 \pm 0.034$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{Cl}^-$	$0.069 \pm 0.046$ ab	$0.127 \pm 0.060$ a	$0.039 \pm 0.035$ b
$\text{F}^-$	$0.037 \pm 0.030$	$0.066 \pm 0.020$	$0.020 \pm 0.016$
$\text{NH}_4^+$	$0.387 \pm 0.135$ b	$0.656 \pm 0.117$ a	$0.479 \pm 0.174$ ab
$\text{Ca}^{2+}$	$0.342 \pm 0.134$	$0.322 \pm 0.049$	$0.314 \pm 0.088$
$\text{Mg}^{2+}$	$0.183 \pm 0.097$	$0.123 \pm 0.032$	$0.109 \pm 0.040$
$\text{Na}^+$	$0.209 \pm 0.123$	$0.174 \pm 0.071$	$0.269 \pm 0.043$
$\text{Zn}^{2+}$	$0.002 \pm 0.001$	$0.003 \pm 0.003$	$0.002 \pm 0.001$
$\text{Fe}^{3+}$	$0.165 \pm 0.105$	$0.110 \pm 0.041$	$0.085 \pm 0.018$
$\text{Mn}^{2+}$	$0.008 \pm 0.003$	$0.007 \pm 0.001$	$0.007 \pm 0.002$
$\text{Pb}^{2+}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.001 \pm 0.001$
$\text{H}^+$	$0.012 \pm 0.023$	$0.167 \pm 0.177$	$0.071 \pm 0.057$
Conductivity	$1.030 \pm 0.360$	$1.838 \pm 0.811$	$0.857 \pm 0.472$
Total anions	0.707	0.739	0.463
Total cations	1.308	1.562	1.337

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

Table 4. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Western White Pine (*Pinus monticola*) - Branches Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.437 \pm 0.145$	$0.495 \pm 0.140$	$0.446 \pm 0.186$
$\text{SO}_4^{2-}$	$0.082 \pm 0.027$	$0.104 \pm 0.041$	$0.121 \pm 0.098$
$\text{PO}_4^{3-}$	$0.034 \pm 0.023$	$0.040 \pm 0.047$	$0.042 \pm 0.049$
$\text{Cl}^-$	$0.038 \pm 0.022 \text{ b}$	$0.383 \pm 0.234 \text{ a}$	$0.031 \pm 0.018 \text{ b}$
$\text{F}^-$	$0.014 \pm 0.003$	$0.063 \pm 0.049$	$0.026 \pm 0.024$
$\text{NH}_4^+$	$0.163 \pm 0.036 \text{ b}$	$0.461 \pm 0.114 \text{ a}$	$0.382 \pm 0.172 \text{ ab}$
$\text{Ca}^{2+}$	$0.302 \pm 0.094$	$0.456 \pm 0.160$	$0.443 \pm 0.120$
$\text{Mg}^{2+}$	$0.142 \pm 0.056$	$0.181 \pm 0.077$	$0.181 \pm 0.062$
$\text{Na}^+$	$0.213 \pm 0.096$	$0.564 \pm 0.344$	$0.223 \pm 0.052$
$\text{Zn}^{2+}$	$0.002 \pm 0.003$	$0.011 \pm 0.009$	$0.002 \pm 0.001$
$\text{Fe}^{3+}$	$0.084 \pm 0.048$	$0.146 \pm 0.090$	$0.128 \pm 0.061$
$\text{Mn}^{2+}$	$0.006 \pm 0.002$	$0.009 \pm 0.003$	$0.010 \pm 0.005$
$\text{Pb}^{2+}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{H}^+$	$0.023 \pm 0.031$	$0.118 \pm 0.109$	$0.027 \pm 0.036$
Conductivity	$0.768 \pm 0.144 \text{ b}$	$1.738 \pm 0.696 \text{ a}$	$1.305 \pm 0.318 \text{ ab}$
Total anions	0.605	1.085	0.666
Total cations	0.935	1.945	1.396

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences the at 0.05 probability level occurred between the results.

Table 5. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Western White Pine (*Pinus monticola*) - Branches Not Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.597 \pm 0.194$	$0.471 \pm 0.116$	$0.386 \pm 0.063$
$\text{SO}_4^{2-}$	$0.116 \pm 0.034$	$0.067 \pm 0.018$	$0.081 \pm 0.043$
$\text{PO}_4^{3-}$	$0.048 \pm 0.033$	$0.067 \pm 0.047$	$0.000 \pm 0.000$
$\text{Cl}^-$	$0.032 \pm 0.011$	$0.085 \pm 0.043$	$0.066 \pm 0.091$
$\text{F}^-$	$0.020 \pm 0.006$	$0.029 \pm 0.008$	$0.026 \pm 0.034$
$\text{NH}_4^+$	$0.271 \pm 0.061$	$0.446 \pm 0.092$	$0.380 \pm 0.056$
$\text{Ca}^{2+}$	$0.411 \pm 0.123$	$0.400 \pm 0.123$	$0.405 \pm 0.031$
$\text{Mg}^{2+}$	$0.216 \pm 0.089$	$0.141 \pm 0.044$	$0.159 \pm 0.020$
$\text{Na}^+$	$0.259 \pm 0.131$	$0.206 \pm 0.089$	$0.248 \pm 0.117$
$\text{Zn}^{2+}$	$0.002 \pm 0.001$	$0.007 \pm 0.007$	$0.002 \pm 0.002$
$\text{Fe}^{3+}$	$0.169 \pm 0.085$	$0.106 \pm 0.034$	$0.119 \pm 0.015$
$\text{Mn}^{2+}$	$0.009 \pm 0.003$	$0.007 \pm 0.002$	$0.008 \pm 0.001$
$\text{Pb}^{2+}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.001 \pm 0.001$
$\text{H}^+$	$0.000 \pm 0.000 \text{ b}$	$0.159 \pm 0.145 \text{ ab}$	$0.256 \pm 0.196 \text{ a}$
Conductivity	$0.825 \pm 0.287$	$1.568 \pm 0.695$	$1.293 \pm 0.540$
Total anions	0.813	0.719	0.559
Total cations	1.337	1.472	1.578

<sup>a</sup> Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

white pine were at the same level, indicating that no significant movement of ions between the interior of the foliage and its surface occurred. Generally, deposition fluxes of the studied ions for this species did not significantly differ from the fluxes determined for the lodgepole pine foliage.

#### B. Deposition to Coulter Pine

Ionic deposition fluxes to the foliage and conductivity of branch rinses for the Coulter pine Teflon-coated branches are presented in Table 6. Generally, deposition fluxes of the investigated ions and conductivity of branch rinses were similar for all of the exposure periods. However, deposition fluxes of fluoride and iron significantly differed between the exposure periods. Deposition fluxes of ions to the foliage and conductivity values for the branches not coated with Teflon are shown in Table 7. Statistically significant differences in deposition fluxes of ammonium, magnesium and sodium between the exposure periods were found. For the remaining ions as well as for conductivity no significant differences between the exposure periods were determined. Higher values of ionic deposition fluxes to the non-Teflon coated foliage compared with the values of the Teflon-coated foliage indicate a possible movement of ions from the needle interior during the rinsing procedures. This difference could also be caused by the reduction of the roughness of needle surfaces through use of a Teflon film increasing the chances of bouncing off the deposited material not adhering to a smooth surface.

The amount of material leached from the foliage interior during the rinsing procedures (extraction correction), was determined by evaluating the deposition fluxes to the Teflon-coated and non-Teflon coated branches of the Coulter pine seedlings enclosed in the particle-free chamber (Tables 8 and 9). Generally, leaching of nitrate, sulfate, phosphate, calcium, and magnesium from the non-Teflon coated foliage was greater than from the Teflon-coated foliage. However, no significant difference in the deposition of other ions between Teflon-coated and non-Teflon coated foliage was determined.

Ionic deposition to the branches and conductivity of branch rinses for the coated and not coated Coulter pine foliage was corrected by subtracting the results from the particle-free chamber, and are presented

Table 6. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Coulter Pine (Pinus coulteri) - Branches Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.774 \pm 0.584$	$0.649 \pm 0.109$	$0.570 \pm 0.159$
$\text{SO}_4^{2-}$	$0.263 \pm 0.212$	$0.299 \pm 0.221$	$0.476 \pm 0.313$
$\text{PO}_4^{3-}$	$0.108 \pm 0.015$	$0.125 \pm 0.084$	$0.178 \pm 0.043$
$\text{Cl}^-$	$0.290 \pm 0.111$	$0.192 \pm 0.051$	$0.135 \pm 0.041$
$\text{F}^-$	$0.121 \pm 0.059 \text{ a}$	$0.044 \pm 0.010 \text{ b}$	$0.031 \pm 0.014 \text{ b}$
$\text{NH}_4^+$	$0.159 \pm 0.070$	$0.340 \pm 0.098$	$0.331 \pm 0.018$
$\text{Ca}^{2+}$	$0.774 \pm 0.305$	$1.043 \pm 0.320$	$1.185 \pm 0.119$
$\text{Mg}^{2+}$	$0.336 \pm 0.281$	$0.282 \pm 0.094$	$0.297 \pm 0.019$
$\text{Na}^+$	$0.963 \pm 0.586$	$0.472 \pm 0.228$	$0.430 \pm 0.087$
$\text{Zn}^{2+}$	$0.016 \pm 0.008$	$0.021 \pm 0.006$	$0.022 \pm 0.006$
$\text{Fe}^{3+}$	$0.080 \pm 0.017 \text{ b}$	$0.094 \pm 0.045 \text{ ab}$	$0.130 \pm 0.011 \text{ a}$
$\text{Mn}^{2+}$	$0.005 \pm 0.001$	$0.008 \pm 0.002$	$0.010 \pm 0.000$
$\text{Pb}^{2+}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{H}^+$	$0.000 \pm 0.000$	$0.056 \pm 0.077$	$0.000 \pm 0.000$
Conductivity	$2.420 \pm 0.761$	$2.925 \pm 0.971$	$1.768 \pm 0.763$
Total anions	1.556	1.309	1.390
Total cations	2.333	2.316	2.405

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

Table 7. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Coulter Pine (*Pinus coulteri*) - Branches Not Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.903 \pm 0.165$	$0.847 \pm 0.239$	$0.607 \pm 0.059$
$\text{SO}_4^{2-}$	$0.655 \pm 0.140$	$0.476 \pm 0.181$	$0.487 \pm 0.313$
$\text{PO}_4^{3-}$	$0.204 \pm 0.079$	$0.215 \pm 0.110$	$0.204 \pm 0.123$
$\text{Cl}^-$	$0.304 \pm 0.147 \text{ a}$	$0.242 \pm 0.013 \text{ ab}$	$0.148 \pm 0.018 \text{ b}$
$\text{F}^-$	$0.080 \pm 0.063$	$0.061 \pm 0.018$	$0.035 \pm 0.004$
$\text{NH}_4^+$	$0.180 \pm 0.036 \text{ b}$	$0.289 \pm 0.054 \text{ a}$	$0.328 \pm 0.037 \text{ a}$
$\text{Ca}^{2+}$	$1.434 \pm 0.168$	$1.448 \pm 0.500$	$1.109 \pm 0.525$
$\text{Mg}^{2+}$	$0.420 \pm 0.048$	$0.319 \pm 0.092$	$0.258 \pm 0.097$
$\text{Na}^+$	$0.663 \pm 0.027 \text{ a}$	$0.397 \pm 0.079 \text{ b}$	$0.399 \pm 0.132 \text{ b}$
$\text{Zn}^{2+}$	$0.014 \pm 0.004$	$0.013 \pm 0.003$	$0.029 \pm 0.010$
$\text{Fe}^{3+}$	$0.120 \pm 0.020$	$0.109 \pm 0.021$	$0.101 \pm 0.019$
$\text{Mn}^{2+}$	$0.008 \pm 0.003$	$0.010 \pm 0.005$	$0.008 \pm 0.002$
$\text{Pb}^{2+}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{H}^+$	$0.000 \pm 0.000$	$0.113 \pm 0.133$	$0.000 \pm 0.000$
Conductivity	$2.905 \pm 0.415$	$2.453 \pm 0.420$	$1.458 \pm 0.823$
Total anions	2.146	1.841	1.481
Total cations	2.839	2.698	2.232

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

Table 8. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Coulter Pine (*Pinus coulteri*) in Clean Air Chambers - Branches Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 21-Aug. 4 1987	Aug. 4-17 1987	Aug. 31-Sept. 15 1987
$\text{NO}_3^-$	$0.110 \pm 0.018$	$0.096 \pm 0.028$	$0.127 \pm 0.024$
$\text{SO}_4^{2-}$	$0.109 \pm 0.034$	$0.068 \pm 0.027$	$0.089 \pm 0.028$
$\text{PO}_4^{3-}$	$0.000 \pm 0.000$	$0.010 \pm 0.020$	$0.036 \pm 0.027$
$\text{Cl}^-$	$0.035 \pm 0.017$	$0.040 \pm 0.028$	$0.044 \pm 0.042$
$\text{F}^-$	$0.015 \pm 0.008$	$0.009 \pm 0.005$	$0.021 \pm 0.025$
$\text{NH}_4^+$	$0.058 \pm 0.025$	$0.036 \pm 0.020$	$0.065 \pm 0.029$
$\text{Ca}^{2+}$	$0.249 \pm 0.106$	$0.152 \pm 0.060$	$0.207 \pm 0.061$
$\text{Mg}^{2+}$	$0.061 \pm 0.004$	$0.039 \pm 0.013$	$0.051 \pm 0.014$
$\text{Na}^+$	$0.051 \pm 0.046$	$0.069 \pm 0.028$	$0.111 \pm 0.060$
$\text{Zn}^{2+}$	$0.010 \pm 0.001$	$0.008 \pm 0.003$	$0.011 \pm 0.005$
$\text{Fe}^{3+}$	$0.015 \pm 0.001$	$0.008 \pm 0.004$	$0.013 \pm 0.005$
$\text{Mn}^{2+}$	$0.001 \pm 0.000$	$0.000 \pm 0.000$	$0.001 \pm 0.001$
$\text{Pb}^{2+}$	$0.001 \pm 0.001$	$0.002 \pm 0.002$	$0.003 \pm 0.003$
$\text{H}^+$	$0.054 \pm 0.053$	$0.004 \pm 0.007$	$0.030 \pm 0.040$
Conductivity	$0.395 \pm 0.031$	$0.100 \pm 0.115$	$0.363 \pm 0.116$
Total anions	0.269	0.223	0.317
Total cations	0.500	0.318	0.491

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

Table 9. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Coulter Pine (*Pinus coulteri*) in Clean Air Chambers - Branches Not Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 21-Aug. 4 1987	Aug. 4-17 1987	Aug. 31-Sept. 15 1987
$\text{NO}_3^-$	$0.330 \pm 0.141$	$0.148 \pm 0.073$	$0.159 \pm 0.051$
$\text{SO}_4^{2-}$	$0.434 \pm 0.229$	$0.146 \pm 0.072$	$0.148 \pm 0.082$
$\text{PO}_4^{3-}$	$0.113 \pm 0.096$	$0.035 \pm 0.050$	$0.058 \pm 0.046$
$\text{Cl}^-$	$0.062 \pm 0.014$	$0.034 \pm 0.020$	$0.029 \pm 0.010$
$\text{F}^-$	$0.036 \pm 0.019$	$0.018 \pm 0.010$	$0.018 \pm 0.015$
$\text{NH}_4^+$	$0.069 \pm 0.008$	$0.047 \pm 0.023$	$0.079 \pm 0.022$
$\text{Ca}^{2+}$	$0.860 \pm 0.437 \text{ a}$	$0.345 \pm 0.197 \text{ b}$	$0.378 \pm 0.186 \text{ b}$
$\text{Mg}^{2+}$	$0.176 \pm 0.077 \text{ a}$	$0.066 \pm 0.034 \text{ b}$	$0.058 \pm 0.015 \text{ b}$
$\text{Na}^+$	$0.144 \pm 0.059$	$0.058 \pm 0.016$	$0.104 \pm 0.023$
$\text{Zn}^{2+}$	$0.014 \pm 0.004$	$0.003 \pm 0.003$	$0.009 \pm 0.001$
$\text{Fe}^{3+}$	$0.018 \pm 0.010$	$0.010 \pm 0.005$	$0.017 \pm 0.004$
$\text{Mn}^{2+}$	$0.002 \pm 0.001$	$0.001 \pm 0.000$	$0.001 \pm 0.000$
$\text{Pb}^{2+}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.005 \pm 0.003$
$\text{H}^+$	$0.010 \pm 0.020$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
Conductivity	$1.055 \pm 0.464 \text{ a}$	$0.370 \pm 0.231 \text{ b}$	$0.335 \pm 0.132 \text{ b}$
Total anions	0.975	0.381	0.412
Total cations	1.293	0.538	0.626

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.



in Tables 10 and 11. Deposition of the studied ions to the two types of foliage are similar, and in the same range as deposition fluxes to the lodgepole and western white pine branches. As was found for the two native pine species, conductivities of the branch rinses for coated and not coated branches, tended to be the highest for the second exposure period.

### C. Deposition to Surrogate Surfaces

Fluxes of ionic dry deposition to nylon filters are presented in Table 12. Significant differences in values of deposition fluxes between the exposure periods were found for chloride, ammonium, calcium and hydrogen ions. Very high deposition fluxes of chloride, sodium and hydrogen and very low deposition fluxes of ammonium ions were also found for this surrogate surface. No significant differences between exposure periods were found for conductivities of filter extracts.

Deposition fluxes of ions to Whatman paper filters and conductivity of filter extracts are presented in Table 13. For nitrate, ammonium, sodium, zinc, hydrogen, as well as for the conductivity, significant differences between the exposure periods were found. Deposition fluxes of ammonium and sodium were very high, while deposition fluxes of phosphate were below detectable limits.

Table 14 shows the comparison of deposition fluxes to all the studied surfaces for pooled data for the entire study. Deposition fluxes of nitrate to paper filters and to coated and non-coated Coulter pine branches were significantly higher than deposition fluxes to the native conifers. The nitrate deposition fluxes to Coulter pine, after the extraction correction, were not different from deposition fluxes to surrogate surfaces and native conifers. Deposition fluxes of sulfate and phosphate to the Coulter pine branches were significantly higher than deposition fluxes to the other surfaces. Deposition fluxes of chloride were the highest to the nylon filters, while deposition fluxes to the conifer branches did not significantly differ. No significant differences in fluoride deposition fluxes were determined for all of the studied surfaces. Exceptionally high deposition of ammonium was determined for

Table 10. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Coulter Pine (*Pinus coulteri*) after Subtracting Values from the Clean Air Chamber ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) - Branches Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.664 \pm 0.584$	$0.553 \pm 0.109$	$0.479 \pm 0.059$
$\text{SO}_4^{2-}$	$0.158 \pm 0.208$	$0.232 \pm 0.221$	$0.387 \pm 0.056$
$\text{PO}_4^{3-}$	$0.108 \pm 0.015$	$0.116 \pm 0.078$	$0.142 \pm 0.043$
$\text{Cl}^-$	$0.255 \pm 0.091 \text{ a}$	$0.152 \pm 0.042 \text{ b}$	$0.091 \pm 0.041 \text{ b}$
$\text{F}^-$	$0.106 \pm 0.049 \text{ a}$	$0.035 \pm 0.008 \text{ b}$	$0.010 \pm 0.015 \text{ b}$
$\text{NH}_4^+$	$0.101 \pm 0.070$	$0.305 \pm 0.098$	$0.266 \pm 0.018$
$\text{Ca}^{2+}$	$0.525 \pm 0.305 \text{ b}$	$0.892 \pm 0.320 \text{ a}$	$0.978 \pm 0.119 \text{ a}$
$\text{Mg}^{2+}$	$0.275 \pm 0.281$	$0.244 \pm 0.094$	$0.246 \pm 0.018$
$\text{Na}^+$	$0.912 \pm 0.586$	$0.403 \pm 0.228$	$0.319 \pm 0.087$
$\text{Zn}^{2+}$	$0.008 \pm 0.008$	$0.016 \pm 0.007$	$0.014 \pm 0.005$
$\text{Fe}^{3+}$	$0.065 \pm 0.017$	$0.086 \pm 0.045$	$0.117 \pm 0.011$
$\text{Mn}^{2+}$	$0.004 \pm 0.001$	$0.008 \pm 0.002$	$0.009 \pm 0.001$
$\text{Pb}^{2+}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{H}^+$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
Conductivity	$2.025 \pm 0.761$	$2.825 \pm 0.971$	$1.405 \pm 0.762$
Total anions	1.287	1.086	1.073
Total cations	1.890	1.954	1.949

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

Table 11. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Branches and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Branch Rinses for Coulter Pine (*Pinus coulteri*) After Subtracting Values from the Clean Air Chamber - Branches not Coated with Teflon<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.573 \pm 0.165$	$0.699 \pm 0.240$	$0.448 \pm 0.059$
$\text{SO}_4^{2-}$	$0.221 \pm 0.141$	$0.330 \pm 0.180$	$0.339 \pm 0.313$
$\text{PO}_4^{3-}$	$0.091 \pm 0.079$	$0.180 \pm 0.110$	$0.146 \pm 0.123$
$\text{Cl}^-$	$0.242 \pm 0.147$	$0.208 \pm 0.011$	$0.119 \pm 0.018$
$\text{F}^-$	$0.047 \pm 0.052$	$0.043 \pm 0.015$	$0.017 \pm 0.004$
$\text{NH}_4^+$	$0.111 \pm 0.036$	$0.243 \pm 0.045$	$0.249 \pm 0.036$
$\text{Ca}^{2+}$	$0.574 \pm 0.169 \text{ b}$	$1.103 \pm 0.500 \text{ a}$	$0.756 \pm 0.525 \text{ b}$
$\text{Mg}^{2+}$	$0.244 \pm 0.047$	$0.253 \pm 0.091$	$0.200 \pm 0.097$
$\text{Na}^+$	$0.519 \pm 0.199$	$0.339 \pm 0.079$	$0.295 \pm 0.132$
$\text{Zn}^{2+}$	$0.000 \pm 0.000$	$0.003 \pm 0.003$	$0.020 \pm 0.011$
$\text{Fe}^{3+}$	$0.102 \pm 0.020$	$0.099 \pm 0.021$	$0.085 \pm 0.019$
$\text{Mn}^{2+}$	$0.006 \pm 0.003$	$0.009 \pm 0.005$	$0.008 \pm 0.002$
$\text{Pb}^{2+}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{H}^+$	$0.000 \pm 0.000$	$0.113 \pm 0.133$	$0.000 \pm 0.000$
Conductivity	$1.850 \pm 0.415$	$2.240 \pm 0.342$	$1.123 \pm 0.823$
Total anions	1.171	1.163	1.069
Total cations	1.556	2.169	1.613

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

Table 12. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{ h}^{-1}$ ) to Nylon Filters and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Filter Extracts<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.542 \pm 0.075$	$0.702 \pm 0.053$	$0.494 \pm 0.208$
$\text{SO}_4^{2-}$	$0.163 \pm 0.040$	$0.044 \pm 0.062$	$0.000 \pm 0.000$
$\text{PO}_4^{3-}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{Cl}^-$	$1.332 \pm 0.233 \text{ b}$	$1.665 \pm 0.798 \text{ b}$	$2.593 \pm 0.413 \text{ a}$
$\text{F}^-$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{NH}_4^+$	$0.147 \pm 0.108 \text{ a}$	$0.024 \pm 0.049 \text{ ab}$	$0.000 \pm 0.000 \text{ b}$
$\text{Ca}^{2+}$	$0.541 \pm 0.130 \text{ b}$	$0.674 \pm 0.236 \text{ b}$	$1.128 \pm 0.200 \text{ a}$
$\text{Mg}^{2+}$	$0.090 \pm 0.039$	$0.022 \pm 0.027$	$0.048 \pm 0.020$
$\text{Na}^+$	$0.922 \pm 0.429$	$1.586 \pm 0.364$	$1.028 \pm 1.130$
$\text{Zn}^{2+}$	$0.022 \pm 0.020$	$0.027 \pm 0.012$	$0.045 \pm 0.030$
$\text{Fe}^{3+}$	$0.068 \pm 0.036$	$0.064 \pm 0.019$	$0.108 \pm 0.031$
$\text{Mn}^{2+}$	$0.006 \pm 0.006$	$0.008 \pm 0.002$	$0.007 \pm 0.009$
$\text{Pb}^{2+}$	$0.032 \pm 0.060$	$0.053 \pm 0.044$	$0.080 \pm 0.096$
$\text{H}^+$	$1.084 \pm 0.255 \text{ b}$	$2.469 \pm 0.207 \text{ a}$	$2.617 \pm 0.729 \text{ a}$
Conductivity	$3.645 \pm 0.647$	$4.830 \pm 1.610$	$4.500 \pm 1.330$
Total anions	2.037	2.411	3.087
Total cations	2.912	4.927	5.061

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

Table 13. Deposition Fluxes of Ions ( $\mu\text{Eq m}^{-2} \text{h}^{-1}$ ) to Whatman Paper Filters and Conductivity ( $\mu\text{mhos cm}^{-1}$  per  $\text{m}^2$  per h) of Filter Extracts<sup>a</sup>

Ion	Period of Exposure		
	July 15-29 1987	Aug. 4-12 1987	Sept. 3-10 1987
$\text{NO}_3^-$	$0.630 \pm 0.175 \text{ b}$	$1.052 \pm 0.276 \text{ a}$	$0.407 \pm 0.113 \text{ b}$
$\text{SO}_4^{2-}$	$0.196 \pm 0.112$	$0.174 \pm 0.093$	$0.100 \pm 0.028$
$\text{PO}_4^{3-}$	$0.000 \pm 0.000$	$0.000 \pm 0.000$	$0.000 \pm 0.000$
$\text{Cl}^-$	$0.397 \pm 0.232$	$0.390 \pm 0.103$	$0.248 \pm 0.060$
$\text{F}^-$	$0.002 \pm 0.005$	$0.024 \pm 0.016$	$0.005 \pm 0.009$
$\text{NH}_4^+$	$1.350 \pm 0.165 \text{ b}$	$1.826 \pm 0.289 \text{ a}$	$1.053 \pm 0.136 \text{ c}$
$\text{Ca}^{2+}$	$0.543 \pm 0.213$	$0.519 \pm 0.097$	$0.450 \pm 0.123$
$\text{Mg}^{2+}$	$0.040 \pm 0.035$	$0.011 \pm 0.015$	$0.013 \pm 0.016$
$\text{Na}^+$	$1.770 \pm 0.316 \text{ a}$	$1.926 \pm 0.289 \text{ a}$	$0.966 \pm 0.220 \text{ b}$
$\text{Zn}^{2+}$	$0.026 \pm 0.008 \text{ a}$	$0.025 \pm 0.014 \text{ ab}$	$0.013 \pm 0.004 \text{ b}$
$\text{Fe}^{3+}$	$0.057 \pm 0.022$	$0.057 \pm 0.027$	$0.035 \pm 0.023$
$\text{Mn}^{2+}$	$0.006 \pm 0.002$	$0.007 \pm 0.003$	$0.002 \pm 0.003$
$\text{Pb}^{2+}$	$0.067 \pm 0.037$	$0.066 \pm 0.031$	$0.033 \pm 0.029$
$\text{H}^+$	$0.000 \pm 0.000 \text{ b}$	$0.110 \pm 0.030 \text{ a}$	$0.284 \pm 0.203 \text{ a}$
Conductivity	$1.530 \pm 0.710 \text{ ab}$	$2.230 \pm 0.620 \text{ a}$	$1.150 \pm 0.250 \text{ b}$
Total anions	1.225	1.640	0.760
Total cations	3.859	4.547	2.849

<sup>a</sup>Means and S.D. for 4 replicate measurements. Results in each row followed by different letters indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

Table 14. Comparison of Deposition Fluxes of Ions ( $\mu \text{Eq m}^{-2} \text{h}^{-1}$ ) to Different Plant and Surrogate Surfaces - Pooled Data for the Entire Study<sup>a</sup>

Ion	Surface									
	Lodgepole Pine Teflon	Lodgepole Pine No Teflon	W. White Pine Teflon	W. White Pine No Teflon	Coulter Pine Teflon	Coulter Pine No Teflon	Coulter Pine Teflon -Clean Chamber	Coulter Pine No Teflon -Clean Chamber	Nylon Filter	Paper Filter
$\text{NO}_3^-$	0.421 b $\pm 0.144$	0.442 b $\pm 0.173$	0.459 b $\pm 0.143$	0.485 b $\pm 0.153$	0.676 a $\pm 0.321$	0.773 a $\pm 0.230$	0.565 ab $\pm 0.322$	0.573 ab $\pm 0.188$	0.579 ab $\pm 0.151$	0.696 a $\pm 0.333$
$\text{SO}_4^{2-}$	0.072 c $\pm 0.026$	0.065 c $\pm 0.035$	0.102 c $\pm 0.060$	0.088 c $\pm 0.037$	0.346 b $\pm 0.189$	0.539 a $\pm 0.220$	0.259 b $\pm 0.189$	0.297 b $\pm 0.210$	0.069 c $\pm 0.081$	0.157 c $\pm 0.088$
$\text{PO}_4^{3-}$	0.000 c $\pm 0.000$	0.015 c $\pm 0.028$	0.038 c $\pm 0.037$	0.038 c $\pm 0.042$	0.136 b $\pm 0.058$	0.208 a $\pm 0.010$	0.122 b $\pm 0.049$	0.139 b $\pm 0.103$	0.000 c $\pm 0.000$	0.000 c $\pm 0.000$
$\text{Cl}^-$	0.063 c $\pm 0.038$	0.078 c $\pm 0.058$	0.151 bc $\pm 0.211$	0.061 c $\pm 0.058$	0.206 bc $\pm 0.087$	0.231 bc $\pm 0.102$	0.166 bc $\pm 0.091$	0.190 bc $\pm 0.094$	1.863 a $\pm 0.739$	0.345 b $\pm 0.154$
$\text{F}^-$	0.029 $\pm 0.014$	0.041 $\pm 0.029$	0.034 $\pm 0.029$	0.025 $\pm 0.019$	0.065 $\pm 0.049$	0.059 $\pm 0.034$	0.050 $\pm 0.050$	0.036 $\pm 0.031$	0.000 $\pm 0.000$	0.010 $\pm 0.014$
$\text{NH}_4^+$	0.448 b $\pm 0.210$	0.507 b $\pm 0.175$	0.335 c $\pm 0.171$	0.366 c $\pm 0.099$	0.277 c $\pm 0.108$	0.266 c $\pm 0.075$	0.224 d $\pm 0.112$	0.201 d $\pm 0.075$	0.057 c $\pm 0.091$	1.410 a $\pm 0.382$
$\text{Ca}^{2+}$	0.356 c $\pm 0.112$	0.326 c $\pm 0.089$	0.400 c $\pm 0.137$	0.405 c $\pm 0.093$	1.001 a $\pm 0.298$	1.330 a $\pm 0.422$	0.798 b $\pm 0.315$	0.811 b $\pm 0.451$	0.781 b $\pm 0.315$	0.504 c $\pm 0.144$
$\text{Mg}^{2+}$	0.132 c $\pm 0.057$	0.138 c $\pm 0.066$	0.168 c $\pm 0.063$	0.172 c $\pm 0.063$	0.305 a $\pm 0.157$	0.332 a $\pm 0.102$	0.255 b $\pm 0.156$	0.232 b $\pm 0.078$	0.053 d $\pm 0.040$	0.021 d $\pm 0.026$

(continued)

Table 14 (continued) - 2

Ion	Surface									
	Lodgepole Pine Teflon	Lodgepole Pine No Teflon	W. White Pine Teflon	W. White Pine No Teflon	Coulter Pine Teflon	Coulter Pine No Teflon	Coulter Pine Teflon -Clean Chamber	Coulter Pine No Teflon -Clean Chamber	Nylon Filter	Paper Filter
Na <sup>+</sup>	0.288 d ± 0.152	0.218 d ± 0.087	0.335 cd ± 0.253	0.238 d ± 0.106	0.622 c ± 0.417	0.486 cd ± 0.154	0.545 cd ± 0.430	0.417 cd ± 0.198	1.179 b ± 0.724	1.554 a ± 0.506
Zn <sup>2+</sup>	0.005 c ± 0.003	0.005 c ± 0.002	0.006 c ± 0.006	0.005 c ± 0.004	0.022 ab ± 0.007	0.018 ab ± 0.010	0.012 c ± 0.007	0.010 c ± 0.010	0.031 a ± 0.022	0.021 b ± 0.011
Fe <sup>3+</sup>	0.099 ab ± 0.055	0.120 ab ± 0.069	0.119 a ± 0.068	0.131 a ± 0.056	0.101 ab ± 0.034	0.110 ab ± 0.020	0.089 ab ± 0.034	0.095 ab ± 0.020	0.080 bc ± 0.034	0.050 c ± 0.024
Mn <sup>2+</sup>	0.007 ± 0.002	0.007 ± 0.002	0.008 ± 0.004	0.008 ± 0.002	0.008 ± 0.003	0.009 ± 0.003	0.007 ± 0.003	0.008 ± 0.003	0.007 ± 0.006	0.005 ± 0.003
Pb <sup>2+</sup>	0.000 b ± 0.000	0.000 b ± 0.000	0.000 b ± 0.000	0.000 b ± 0.000	0.000 b ± 0.000	0.000 b ± 0.000	0.000 b ± 0.000	0.000 b ± 0.000	0.055 a ± 0.020	0.055 a ± 0.025
H <sup>+</sup>	0.094 b ± 0.132	0.083 b ± 0.118	0.056 b ± 0.077	0.138 b ± 0.168	0.019 b ± 0.049	0.038 b ± 0.089	0.000 b ± 0.000	0.038 b ± 0.089	2.057 a ± 0.834	0.131 b ± 0.162
Conduc- tivity	1.270 c ± 0.687	1.276 c ± 0.695	1.263 c ± 0.624	1.228 c ± 0.580	2.371 b ± 0.905	2.255 b ± 0.852	2.085 b ± 0.971	1.738 bc ± 0.706	4.325 a ± 1.256	1.637 bc ± 0.690

<sup>a</sup>Means and S.D. for 12 pooled measurements for the three exposure periods. Different letters following means in row indicate significant differences at the 0.05 probability level (mean values decrease in an alphabetical order). Absence of letters indicates that no significant differences at the 0.05 probability level occurred between the results.

<sup>b</sup>Conductivity units are  $\mu\text{mhos cm}^{-1} \text{ m}^{-2} \text{ h}^{-1}$ .

the paper filters, however, deposition fluxes to Coulter pines, after the extraction correction, were lower than to the native pines. Deposition fluxes of calcium to nylon filters and Coulter pines, after the extraction correction, were significantly higher than to the native conifers and Whatman filters. Deposition fluxes of magnesium to Coulter pines were significantly higher than to the native conifers and surrogate surfaces. The sodium deposition fluxes to the filters were significantly greater than to the conifers. Deposition fluxes of zinc and iron to the conifers did not significantly differ. No deposition of lead was determined for the conifers - deposition fluxes of lead to the nylon and paper filters were at the same level. The highest deposition of hydrogen ions was determined for the nylon filters - deposition fluxes to the other surfaces did not significantly differ. The highest conductivity values were determined also for the nylon filters - conductivity values were the lowest for the native conifers.

Simple correlations between ionic deposition fluxes and between studied surfaces were calculated using Waller-Duncan's correlation test (Steel and Torrie, 1980). Deposition of nitrate was strongly correlated with depositions of sulfate and calcium. Sulfate deposition was also strongly correlated with deposition of phosphate and magnesium. Interestingly, ammonium deposition was not correlated with deposition of nitrate or sulfate and the sum of these ions. It would indicate that deposition of this ion was probably a product of ammonia gas transported from the San Joaquin Valley (Table 15). Deposition of ions to the coniferous surfaces were in all cases strongly intercorrelated. However, in only a few cases was deposition of ions to surrogate surfaces strongly correlated with depositions to the conifers (Table 16).



Table 15. Simple correlations between ionic deposition fluxes-pooled data for all the studied surfaces and three exposure periods<sup>a</sup>

	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	Cl <sup>-</sup>	F <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Zn <sup>2+</sup>	Fe <sup>3+</sup>	Mn <sup>2+</sup>	H <sup>+</sup>	Cond.
NO <sub>3</sub>	1.000													
SO <sub>4</sub> <sup>2-</sup>	0.799**	1.000												
PO <sub>4</sub> <sup>3-</sup>	0.615*	0.950**	1.000											
Cl <sup>-</sup>	0.169	-0.208	-0.277	1.000										
F <sup>-</sup>	0.185	0.676*	0.777**	-0.559	1.000									
NH <sub>4</sub> <sup>+</sup>	0.185	-0.194	-0.405	-0.243	-0.437	1.000								
Ca <sup>2+</sup>	0.830**	0.914**	0.858**	0.192	0.500	-0.370	1.000							
Mg <sup>2+</sup>	0.344	0.813**	0.920**	-0.442	0.936**	-0.533	0.682*	1.000						
Na <sup>+</sup>	0.554	-0.023	-0.250	0.591*	-0.617*	0.540	0.155	-0.539	1.000					
Zn <sup>2+</sup>	0.704*	0.290	0.112	0.770**	-0.249	0.011	0.580*-0.125	0.797**	1.000					
Fe <sup>3+</sup>	-0.463	-0.021	0.178	-0.409	0.511	-0.540	-0.130	0.461	-0.873**	-0.634*	1.000			
Mn <sup>2+</sup>	0.069	0.523	0.673*	-0.183	0.672*	-0.759**	0.496	0.790**	-0.677*	-0.194	0.749**	1.000		
H <sup>+</sup>	0.016	-0.333	-0.376	0.983**	-0.592*	-0.286	0.070	-0.492	0.485	0.661*	-0.295	-0.163	1.000	
Cond.	0.416	0.138	0.071	0.919**	-0.236	-0.380	0.522	-0.098	0.546	0.882**	-0.401	-0.003	0.862**	1.000

<sup>a</sup>n=12; \*, \*\* - correlations significant at  $p \leq 0.05$  and  $\leq 0.01$ , respectively.

Table 16. Simple correlations between the studied surfaces-pooled data for all the studied ions and three exposure periods<sup>a</sup>

	LPT <sup>b</sup>	LPNT	WPT	WPNT	CPT	CPNT	CPT-C	CPNT-C	NYLON	PAPER
LPT <sup>b</sup>	1.000									
LPNT	0.996**	1.000								
WPT	0.990**	0.982**	1.000							
WPNT	0.993**	0.989**	0.991**	1.000						
CPT	0.943**	0.928**	0.974**	0.958**	1.000					
CPNT	0.904**	0.884**	0.936**	0.927**	0.983**	1.000				
CPT-C	0.952**	0.932**	0.977**	0.960**	0.999**	0.976**	1.000			
CPNT-C	0.939**	0.920**	0.969**	0.955**	0.997**	0.992**	0.995**	1.000		
NYLON	0.764*	0.742*	0.784**	0.765*	0.775**	0.714*	0.782**	0.765*	1.000	
PAPER	0.803**	0.787**	0.783**	0.750*	0.702*	0.632	0.706*	0.678*	0.572	1.000

<sup>a</sup>n=12; \*, \*\* - correlations significant at  $p \leq 0.05$  and  $0.01$ , respectively.

<sup>b</sup>LPT-Lodgepole pine coated with Teflon.

LPNT-Lodgepole pine not coated with Teflon.

WPT-Western white pine coated with Teflon.

WPNT-Western white pine not coated with Teflon.

CPT-Coulter pine coated with Teflon.

CPNT-Coulter pine not coated with Teflon.

CPT-C-Coulter pine coated with Teflon corrected for leaching.

CPNT-C-Coulter pine not coated with Teflon corrected for leaching.

NYLON-Nylasorb nylon filters.

PAPER-Whatman paper filters.

#### IV. DISCUSSION

No direct verification of ionic deposition by a comparison with deposition at other similar locations was possible as there have been no other studies on dry deposition to vegetation in the Sierra Nevada. However, results of deposition fluxes of some of the studied ions can be compared with studies performed elsewhere. Nitrate deposition fluxes were low compared with the results of dry deposition fluxes determined with leaf washing techniques for other areas. Deposition fluxes to Ceanothus crassifolius and nylon filters at Tanbark Flat in the San Gabriel Mountains of the South Coast Air Basin in the summer of 1985 were several fold greater than those at Emerald Lake [in the ranges of 1.42 - 7.34 for C. crassifolius, and 1.65 - 9.11  $\mu\text{Eq m}^{-2} \text{h}^{-1}$  for nylon filters (Bytnerowicz et al., 1987a)]. However, dry deposition fluxes of nitrogen compounds at Tanbark Flat were very high due to high levels of nitrogen compounds emissions in that area (Bytnerowicz et al., 1987b).

A very recent study (Appendix), showed that ionic fluxes to potted seedlings of P. coulteri at Emerald Lake were at a similar level as at Tanbark Flat. However, deposition fluxes of nitrate and hydrogen ions to nylon filters was several times greater at Tanbark Flat than at Emerald Lake. The same study also indicated that atmospheric deposition of ions to native pines was several times greater at Emerald Lake than at Eastern Brook Lake (eastern Sierra Nevada). Deposition fluxes of nitrate to the foliage of a conifer species (Austrian pine) north of Detroit, Michigan were much higher than the values at the Emerald Lake location, but similar to the values from Tanbark Flat [about 7.1  $\mu\text{Eq m}^{-2} \text{h}^{-1}$  at the perimeter of the stand, and 2.1  $\mu\text{Eq m}^{-2} \text{h}^{-1}$  in the stand interior] (Dasch, 1986).

The differences between sulfate and phosphate deposition fluxes to native pines and Coulter pine may be due to differences in the surface structure of their needles. Coulter pine needles may be rougher due to a relatively thin layer of cuticular waxes. Lodgepole and western white pines grown at high altitudes of the Sierra Nevada may have a thick wax layer, giving them a smooth appearance. Deposition velocities, which determine fluxes of aerosol particles to surfaces, depend strongly on the roughness of surfaces (Hosker and Lindberg, 1982). Sulfate aerosol particles are smaller in size than the nitrate aerosols (Orel and

Seinfeld, 1977), therefore their deposition may be more dependent on the roughness of surfaces to which they are deposited. Deposition fluxes of sulfate to different surfaces at Emerald Lake were several times lower than to Ceanothus crassifolius foliage and nylon filters at Tanbark Flat [0.16 - 0.89 and 1.07 - 2.44  $\mu\text{Eq m}^{-2} \text{h}^{-1}$ , respectively] (Bytnerowicz et al., 1987a). They were also much lower than the values determined for the pine foliage on the perimeter and interior trees in the Michigan forest stand [2.59 and 0.62  $\mu\text{Eq m}^{-2} \text{h}^{-1}$ , respectively] (Dasch, 1986).

Calcium deposition fluxes to Coulter pine and to the filters at Emerald Lake were in the same range as fluxes to chestnut oak trees and polycarbonate Petri dishes studied in the Walker Branch Watershed in Tennessee (Lindberg and Lovett, 1983; 1985); however, deposition fluxes to the native conifers were significantly lower.

No studies on deposition of the remaining ions to plant surfaces have been done, so no comparisons with other studies were possible. Obviously more studies on deposition of ions to plant surfaces are needed. Balancing sums of cation and anion fluxes for each of the surfaces revealed substantial deficits of anion fluxes. Such a deficit was not found on the eastern side of the Sierra Nevada (Appendix). The most probable reason for this is that no carbonate and organic anions were determined in this study. It has already been suggested that organic components such as acetic, butyric, formic, lactic, succinic, glycolic, propionic and isocitric acids (Shriner, 1979) may play an important role in atmospheric deposition.

The ratios of nitrate:sulfate and ammonium:sulfate deposition fluxes (chemical equivalents) to plants and surrogate surfaces at Emerald Lake and other locations are presented in Table 17. These results indicate that, at Emerald Lake, the dry deposition of nitrate and ammonium to native conifers is greater than deposition of sulfate, similar to what has been found in the San Gabriel Mountains of the South Coast Air Basin. However, at Emerald Lake the participation of ammonium in the total load of nitrogen dry deposition is higher than at Tanbark Flat. This situation is probably caused by a transport of ammonia and ammonium aerosols from the farmlands of the San Joaquin Valley. The proportion of nitrogen to sulfur deposited to the native conifers at Emerald Lake is higher than in

Table 17. Ratios of Nitrate:Sulfate and Ammonium:Sulfate Deposition Fluxes (Chemical Equivalents) to Plant and Surrogate Surfaces in Different Locations

Site	Type of Surface	$\text{NO}_3^-:\text{SO}_4^{2-}$	$\text{NH}_4^+:\text{SO}_4^{2-}$	Reference
Emerald Lake Sequoia National Park, California	<u>Pinus concorta</u> non-Teflon coated	7.3	8.5	This work
	<u>Pinus concorta</u> Teflon coated	6.0	6.4	
	<u>Pinus menticola</u> non-Teflon coated	5.3	4.1	
	<u>Pinus menticola</u> Teflon coated	4.6	3.3	
	<u>Pinus coulteri</u> non-Teflon coated	1.9	1.0	
	<u>Pinus coulteri</u> Teflon coated	2.3	1.0	
	<u>Pinus coulteri</u> , non-Teflon coated, corrected for ion extraction from needle interior	1.9	0.7	
	<u>Pinus coulteri</u> , Teflon coated, corrected for ion extraction from needle interior	2.2	0.9	
	Nylon Filters	8.0	0.9	
Tanbark Flat San Gabriel Mountains, California	Paper Filters	4.4	9.1	Bytnerowicz et al. (1987a)
	<u>Ceanothus</u> <u>crassifolius</u>	9.5	4.5	
	Nylon filters	3.6	1.4	
	Petri dishes	3.1	0.7	

(continued)

Table 17 (continued) - 2

Site	Type of Surface	$\text{NO}_3^-:\text{SO}_4^{2-}$	$\text{NH}_4^+:\text{SO}_4^{2-}$	Reference
Warren Michigan	<u>Quercus</u> sp. perimeter of a stand, branch	2.1	ND	Dasch (1986)
	<u>Quercus</u> sp. interior of a stand, branch	2.0	ND	
Lapeer County Michigan	<u>Pinus</u> sp. perimeter of a stand, branch	5.0	2.1	Dasch (1986)
	<u>Pinus</u> sp., interior of a stand, branch	3.4	2.1	
Walker Branch Watershed, Tennessee	<u>Quercus prinus</u> and <u>Quercus</u> <u>alba</u> branches	0.3	0.2	Lindberg et al. (1986)

ND - not detected.

the Michigan forest locations (Dasch, 1986), and much higher than in the Walker Branch Experimental Forest in Tennessee (Lindberg et al., 1986). A proportion of nitrate and ammonium to sulfate in materials deposited to the lodgepole and western white pines as well as to nylon and paper filters is much higher than in wet deposition measured at Giant Forest of the Sequoia National Park (Stohlgren and Parsons, 1987).

High levels of chloride deposition were detected in the Emerald Lake area. The origin of this deposition may be the burning of vegetation in the San Joaquin Valley, as well as transport of marine air from the Pacific Ocean. Transport of chlorides over long distances is quite possible - high concentrations of chloride in dry deposition originating from the Pacific Ocean were found in Wisconsin, Kansas, Missouri, Kentucky, Indiana and Ohio (Shaw, 1987). High concentrations of chloride in wet precipitation were also detected at Giant Forest, Sequoia National Park (Stohlgren and Parsons, 1987).

Additional work on the development of the method of dry deposition determinations is of great importance. Teflon coating of the foliage seem to help in preventing the movements of the ions between the interior and surface of the foliage. This procedure reduces the experimental error caused by a possible uptake of nutrients deposited on the surface of the foliage by its interior during the exposure periods. It also reduces leakage of nutrients from the interior of the foliage during the washing procedures. However, such coating may change the roughness of needle surfaces, which in turn may increase nutrient fallout from the foliage, especially in strong winds. Other means of preventing ion movement between foliage surface and its interior should be investigated. Scanning electron microscopy examination of plant surfaces should be added to future studies. Closer examination of plant foliage coated with different materials, as well as use of particle-free chambers should lead to precise and direct assessments of dry deposition fluxes to plant canopies.

Evaluation of dry deposition with use of surrogate surfaces for a wide spectrum of atmospheric ions seems to be almost impossible as it is very difficult to simulate natural plant surfaces. Even comparisons between deposition fluxes to foliage of different coniferous species is difficult, as shown by the comparisons of sulfate, phosphate or ammonium deposition fluxes to native pines and Coulter pine in this study.

Surrogate surfaces seem to attract particular ions with different efficiencies. However, if artificial surfaces are used, more information on boundary layer differences between them and natural plant surfaces is essential. In addition, a characterization of chemical attraction between surrogate surfaces and atmospheric ions is desirable.



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V. APPENDIX

ATMOSPHERIC DRY DEPOSITION TO CONIFERS AND SURROGATE  
SURFACES IN THE SIERRA NEVADA AND SAN GABRIEL MOUNTAINS \*, \*\*

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### Abstract

Fluxes of atmospheric dry deposition ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{H}^+$ ) to native pines, potted pine seedlings and filter and nylon filters at Eastern Brook Lake (eastern Sierras), Emerald Lake (western Sierras), and Tanbark Flat (San Gabriel Mountains) were determined in summer 1987. Deposition fluxes of most of ions to *Pinus concorta* and *P. monticola* at Emerald Lake were several times higher than the fluxes to *P. concorta* and *P. albicaulis* at Eastern Brook Lake. Deposition fluxes of ions to potted seedlings of *P. coulteri* at Emerald Lake were at the same level as the fluxes at Tanbark Flat. Results from nylon filters indicated highest deposition fluxes of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  at Tanbark Flat - for  $\text{NO}_3^-$  and  $\text{H}^+$  this phenomenon was also confirmed for paper filters. A substantial deficit of anions was found in dry deposition at Emerald Lake, indicating a possibility of deposition of organic anions of anthropogenic origin.



## Introduction

Atmospheric dry deposition is an important process of ionic transfer in many environments. In humid forests of the southeastern United States, 19 to 64% of the total annual deposition of Ca, Na, K and Mg, as well as up to 89% of P can be delivered through dryfall. Input of ions to ecosystems may be even more important in western United States, where in many areas wet atmospheric deposition in summer is scarce, and soils are poor in nutrients. Atmospheric dry deposition is especially important in chaparral ecosystems of southern California. Studies in the San Gabriel Mountains of the South Coast Air Basin revealed that large amounts of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are deposited as dryfall to these ecosystems<sup>2,3,4,5,6</sup>. This situation is caused by high concentrations of  $\text{NO}_x$ , particulate  $\text{NO}_3^-$ ,  $\text{HNO}_3$  vapor and particulate  $\text{NH}_4^+$  in the air of that area. The relative importance of N compounds in dry deposition in western United States is different from the situation in eastern United States and central Europe, where S compounds play a more important role in atmospheric dry and wet deposition<sup>8,9,10</sup>. Although dry deposition is considered to be an important component of ionic input to ecosystems in the Sierra Nevada Mountains<sup>11</sup>, very little research has been conducted on this subject. Yet, information on the levels of atmospheric dry deposition of ions to forest ecosystems is of great importance because of its potential influence on plant health, biomass production, nutrient balance, nutrient cycling and fuel accumulation rates. In this study ionic deposition to native conifers, potted pine seedlings and surrogate surfaces in the subalpine environment of western and eastern Sierra Nevada Mountains as well in the chaparral ecosystem of the San Gabriel Mountains of southern California were determined. Results of this study can serve as a basis for planning more intensive studies on the effects of atmospheric dry deposition on forest ecosystems in California mountains.

## Materials and Methods

### Study sites:

The study was performed in three sites: Eastern Brook Lake in the eastern Sierra Nevada Mountains, Emerald Lake of the Sequoia National Park in the western Sierra Nevada Mountains, and Tanbark Flat of the San Dimas Experimental Forest in the San Gabriel Mountains (Figure 1). Altitudes of these sites are as follows: Eastern Brook Lake - 3100 m, Emerald Lake - 2740 m, and Tanbark Flat - 800 m.

### Time of the study:

Collection of atmospheric deposition to plant and surrogate surfaces was performed in summer of 1987 during periods without any wet precipitation. Dry deposition was collected: at Eastern Brook Lake during July 27-August 10, and August 10-24, at Emerald Lake during July 15-30, August 4-12, and September 3-10, and at Tanbark Flat during July 21-August 3, and August 17-31 periods.

### Collection of dry deposited materials:

Atmospheric dry deposition to three native pine species, one species of a potted pine, and two surrogate surfaces were determined.

Native pines. At Eastern Brook Lake lodgepole pine (*Pinus contorta*) and whitebark pine (*P. albicaulis*), and at Emerald Lake *P. contorta* and western white pine (*P. monticola*) were used for the study. At Eastern Brook Lake three, and at Emerald Lake four trees (15-30 cm in diameter at breast height) of each species were

selected. Two branches 5-10 cm long on each of the selected trees were thoroughly washed with distilled-deionized water dispersed from plastic spray bottles. When dry, one of the branches on each tree was sprayed with Teflon film (to prevent movement of ions between the surface and interior of the foliage during exposure periods, and leaching of ions from the leaf interior during the rinsing procedures). The other washed branch on each tree was not coated with Teflon. At the end of each exposure period the branches were rinsed with about 80 mL of distilled-deionized water. The rinsing solutions were collected in the 130 mL plastic bottles and immediately placed in cool-boxes filled with dry ice. The samples were kept frozen (-18°C) prior to the analysis. At the end of the study the branches were cut, and surface areas of the needles and twigs were determined.

Potted pines. Four 2-year old seedlings of Coulter pine (*P. coulteri*) in pots were placed in the vicinity of the native pines at Eastern Brook Lake and Emerald Lake, and on the heliport at Tanbark Flat. As for the native pines, two branches on each tree were selected and prepared for dry deposition collection. Four seedlings of similar appearance were placed in the aerosol-free chamber located in Riverside. Rinsing of the needles enclosed in the particle-free chamber was used to determine the amount of material extracted from the needle interior during the washing procedures. At the end of each exposure period the *P. coulteri* branches were rinsed as described above for the native pines. After the rinses were finished, the branches were cut, and their surface areas determined.

Surrogate Surfaces. Nylon filters (Nylasorb 1.0 micrometer pore-size and 47 mm in diameter) and paper filters (Whatman No. 41, 47 mm in diameter) were held in nylon double rings at about 50 cm above the ground. Both surrogate surfaces were exposed in a horizontal position. Four filters of each kind were placed in the vicinity of potted *P. coulteri* seedlings at each study site. The filters were changed at the same time as the conifer branches were rinsed. The exposed filters were placed in 60 mm diameter Petri dishes and were additionally enclosed in tightly closed plastic bags. Immediately after the collection the filters were placed in cool-boxes filled with dry ice. Prior to the extraction the filters were kept at -18°C.

#### Chemical Analysis:

The foliage rinses were thawed and brought up to 100 mL volume. Nylon and paper filters were placed in 250 mL Erlenmeyer flasks with 100 mL of distilled-deionized water and extracted for 15 min on an automatic laboratory shaker. The extracts were filtered and pH of foliage rinses and filter extracts were immediately measured with a Ross electrode and Orion Ionalyzer. Concentrations of metallic cations were determined with by inductively coupled plasma (ICP) analysis (modified Applied Research Laboratory instrument). Concentrations of anions were determined by ion chromatography (Dionex 2010 Ion Chromatograph) and concentrations of  $\text{NH}_4^+$  were determined colorimetrically (Technicon Autoanalyzer II).

### Results and Discussion

#### Deposition to Native Pines:

No significant differences in dry deposition fluxes to branches of native conifers coated with Teflon, and non-Teflon coated were found. This may indicate that



there was no uptake of ions through surfaces during exposure periods, and that no leaching of ions from the foliage interior during the rinsing procedures occurred. Another possibility is that while these two processes occurred, they were in equilibrium resulting in the same deposition fluxes for both types of the surfaces. Therefore only the results of deposition rates to non-Teflon coated branches are presented. Average deposition of air-borne  $\text{NO}_3^-$  to Pinus concorta branches at Emerald Lake was 4.8 X greater than at Eastern Brook Lake. Deposition of  $\text{SO}_4^{2-}$  at Emerald Lake was 2.3 X greater than at Eastern Brook Lake. Deposition of  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and  $\text{F}^-$  at two locations were at the same level. Much higher values of cation deposition to P. concorta were determined at Emerald Lake than at Eastern Brook Lake: for  $\text{NH}_4^+$  5.6 X,  $\text{Ca}^{2+}$  4.0 X,  $\text{Mg}^{2+}$  3.5 X,  $\text{Na}^+$  12.8 X,  $\text{Fe}^{3+}$  4.1 X, and  $\text{Mn}^{2+}$  3.5 X. No  $\text{H}^+$  deposition to P. concorta was found at Eastern Brook Lake, while at Emerald Lake average deposition of  $\text{H}^+$  was  $0.083 \mu\text{Eq m}^{-2} \text{h}^{-1}$  (Figure 2). In Figure 3 comparison of deposition fluxes between P. albicaulis at Eastern Brook Lake and P. monticola at Emerald Lake is presented. These two species have been compared because their needles have similar geometry, and both conifers have 5 needles in a fascicle. As observed for P. concorta, deposition rates of most ions at Emerald Lake were several times greater than at Eastern Brook Lake:  $\text{NO}_3^-$  6.8 X,  $\text{SO}_4^{2-}$  2.7 X,  $\text{PO}_4^{3-}$  4.2 X,  $\text{NH}_4^+$  5.1 X,  $\text{Ca}^{2+}$  4.1 X,  $\text{Mg}^{2+}$  4.1 X,  $\text{Na}^+$  7.9 X,  $\text{Fe}^{3+}$  4.7 X and  $\text{Mn}^{2+}$  4.0 X. No deposition of  $\text{H}^+$  was determined for P. albicaulis at Eastern Brook Lake, and at Emerald Lake deposition of  $\text{H}^+$  to P. monticola was  $0.138 \mu\text{Eq m}^{-2} \text{h}^{-1}$ . Deposition rates of ions to P. albicaulis and P. concorta at Eastern Brook Lake were alike. At Emerald Lake deposition rates to P. monticola and P. concorta were similar as well. At Eastern Brook Lake the sums of anion and cation depositions were equal for either native conifer species. At Emerald Lake there was a surplus of deposited cations to branches of either native conifers.

Deposition to potted P. coulteri. Deposition fluxes of ions to non-Teflon coated branches of potted P. coulteri were higher than to Teflon coated branches at all the sites. This indicated leaching of ions from the foliage interior during rinsing procedures and lack of uptake of ions deposited on foliage surface to its interior. In addition deposition fluxes of ions for the non-Teflon coated branches were always higher than for the Teflon coated ones in the clean air chamber. This confirms an assumption that during rinsing procedures leaching of ions from the needle interior takes place, and that Teflon coating does not totally prevent this process. However, after subtracting values of deposition fluxes in the clean-air chamber from the values of deposition fluxes on the field, the values for both Teflon coated and non-Teflon coated branches did not significantly differ. Therefore only the results from the non-Teflon coated branches are presented. As for the native pines, there was a big difference in deposition fluxes between Eastern Brook Lake and Emerald Lake sites. For the non-Teflon coated branches deposition of the anions (except  $\text{F}^-$ ) at Emerald Lake was greater than at Eastern Brook Lake:  $\text{NO}_3^-$  2.7 X,  $\text{SO}_4^{2-}$  1.6 X,  $\text{PO}_4^{3-}$  1.9 X, and  $\text{Cl}^-$  2.4 X. Also deposition fluxes of cations at Emerald Lake were higher than at Eastern Brook Lake:  $\text{NH}_4^+$  4.8 X,  $\text{Ca}^{2+}$  2.1 X,  $\text{Mg}^{2+}$  2.6 X,  $\text{Na}^+$  5.5 X,  $\text{Zn}^{2+}$  3.8 X,  $\text{Fe}^{3+}$  3.1 X, and  $\text{Mn}^{2+}$  3.0 X. At Emerald Lake deposition of  $\text{H}^+$  was  $0.038 \mu\text{Eq m}^{-2} \text{h}^{-1}$ , while no  $\text{H}^+$  deposition was determined at Eastern Brook Lake. Deposition of some ions to P. coulteri at Emerald Lake was higher than at Tanbark Flat:  $\text{SO}_4^{2-}$  1.8 X,  $\text{PO}_4^{3-}$  2.6 X,  $\text{Cl}^-$  1.5 X,  $\text{Ca}^{2+}$  1.6 X,  $\text{Na}^+$  1.3 X,  $\text{Fe}^{3+}$  1.5, and  $\text{Mn}^{2+}$  1.5 X. However, deposition flux of  $\text{H}^+$  was 1.9 fold greater at Tanbark Flat than at Emerald Lake. Similarly as for the native conifers, there was a balance between anions and cations deposited to P. coulteri at Eastern Brook Lake. At Emerald Lake and Tanbark Flat the sum of cations was greater than the sum of anions

(Figure 4). Similar trend was preserved for the Emerald Lake plants when deposition fluxes determined in the clean-air chamber were subtracted from the fluxes determined in the study site. However, for the Eastern Brook Lake and Tanbark Flat pines the cation/anion ratios decreased (Figure 5). Deposition fluxes to P. coulteri at Tanbark Flat were several times lower than deposition fluxes to Ceanothus crassifolius (a chaparral species) determined in 1985<sup>6</sup>.

#### Deposition to surrogate surfaces:

Comparison of deposition fluxes to nylon filters at Eastern Brook Lake and Emerald Lake confirms the trends previously described for the pine branches: much greater fluxes of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{H}^+$  at the Emerald Lake site. A similar tendency was seen for the paper filters, however the differences between sites were smaller. Deposition fluxes of  $\text{NO}_3^-$  and  $\text{H}^+$  to nylon and paper filters at Tanbark Flat were similar to the values determined in 1985 at the same site<sup>6</sup>, and were much higher than at Emerald Lake. High values for  $\text{NO}_3^-$  and  $\text{H}^+$  deposition to the filters were different from the results for the P. coulteri. A possible explanation for these differences may be a greater efficiency of the filters than plant surfaces in absorbing  $\text{HNO}_3$  vapor occurring in high concentrations in the San Gabriel Mountains<sup>7</sup>. Deposition fluxes of  $\text{SO}_4^{2-}$  to nylon filters also were the highest at Tanbark Flat, but  $\text{SO}_4^{2-}$  deposition to paper filters were similar at all sites (Table 1).

#### Significance of Differences in Deposition Between Sites:

Results of deposition fluxes to native pines and potted P. coulteri at Eastern Brook Lake and Emerald Lake sites indicate a much higher input of anions as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  on the western side of the Sierras than on the eastern side.<sup>3</sup> For  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  these differences were confirmed by the data from the nylon filters, and to a smaller extent also from the paper filters. Higher deposition fluxes to native conifers and potted P. coulteri on the western vs. eastern side of the Sierra Nevada Mountains was even more pronounced for such cations as  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ . Higher deposition of ions to conifers on the western side of the Sierras is probably caused by a westward movement of particulate aerosols with polluted air masses coming from the San Joaquin Valley, where relative high air pollution concentrations have been reported<sup>12</sup>. Effects of increased ionic input to the Sierra Nevada forests are difficult to assess. The effects may be beneficial due to addition of nutrients to poor granite soils. However, with increased load of N species to ecosystems a possibility of longer vegetative growth of trees may be expected, which in turn can lead to higher susceptibility to frost damage<sup>13</sup>. With increasing concentrations of  $\text{O}_3$  and other toxic air pollutants trees may therefore experience a complex anthropogenic stress. The importance of N compounds in dry deposition to native trees at Emerald Lake may also be seen comparing  $\text{NO}_3^-/\text{SO}_4^{2-}$  and  $\text{NH}_4^+/\text{SO}_4^{2-}$  ratios at different locations (Table 2). These ratios were the highest at Tanbark Flat for C. crassifolius and at Emerald Lake for the two native pines. The  $\text{NO}_3^-/\text{SO}_4^{2-}$  and  $\text{NH}_4^+/\text{SO}_4^{2-}$  ratios for native pines at Eastern Brook Lake were at the similar level as the ratios for Quercus and Pinus species in Michigan, but much higher than the ratios for Q. prinus and Q. alba in Tennessee.

#### Cation/Anion Balance:

Another important aspect of the results of dry deposition to conifers is the surplus of cations on the western side of the Sierras. Such a situation was not found on the eastern side of the Sierras. A possible explanation for this

phenomenon may be deposition of organic ions. High concentrations of organic acids in throughfall at Emerald Lake has been reported<sup>16</sup>. It has been reported that organic acids may play an important role in atmospheric deposition<sup>17</sup>. With increasing anthropogenic pollution pressure an increase of formic and acetic acid (products of oxidation of aldehydes emitted from automobile engines) concentrations in the air of the San Joaquin Valley may be expected. No deposition of  $H^+$  to plant surfaces was determined at Eastern Brook Lake, but was detected at Emerald Lake and Tanbark Flat. The presented data indicate that polluted air from the San Joaquin Valley reaches the subalpine environment of western Sierra Nevada Mountains, and that Los Angeles Basin air is transferred to the San Gabriel Mountains causing increased deposition of ions to forest ecosystems. On another hand, air masses reaching subalpine environment of Eastern Brook Lake (coming in summer mostly from the S-W direction) evidently have low concentrations of pollutants resulting in low deposition values. Based on the equilibrium between anions and cations no significant deposition of organic acid anions to the the eastern Sierra Nevada forest ecosystem is expected.

### Conclusions

1. Atmospheric dry deposition of ions to native pines in a subalpine environment was several times greater on the western side than on the eastern side of the Sierras. Based on results of atmospheric deposition to potted P. coulteri, ionic fluxes in the western Sierras are at the similar level as in the San Gabriel Mountains of southern California.
2. Materials deposited to native and potted pines in the western Sierras are rich in N compounds and  $H^+$ . Because of the importance of N species as plant nutrients and air pollutants, monitoring of a wide spectrum of N compounds ( $NO_x$ ,  $NH_3$ ,  $HNO_3$ , particulate  $NO_3$ , PAN etc.) is recommended.
3. A deficit of anions compared to cations in dry deposition at Emerald Lake indicates a possibility of a substantial deposition of organic ions transported from the San Joaquin Valley. Input of organic acids to the forest environment of the Sierra Nevada Mountains should be investigated.
4. Results from nylon filters indicate highest deposition of  $NO_3^-$ ,  $SO_4^{2-}$  and  $H^+$  at Tanbark Flat - for  $NO_3^-$  and  $H^+$  this phenomenon was also confirmed for paper filters. Nylon and paper filters attract particular atmospheric ions with different efficiencies. A possibility of using artificial surfaces as indicators of deposition to vegetation has to be carefully examined.

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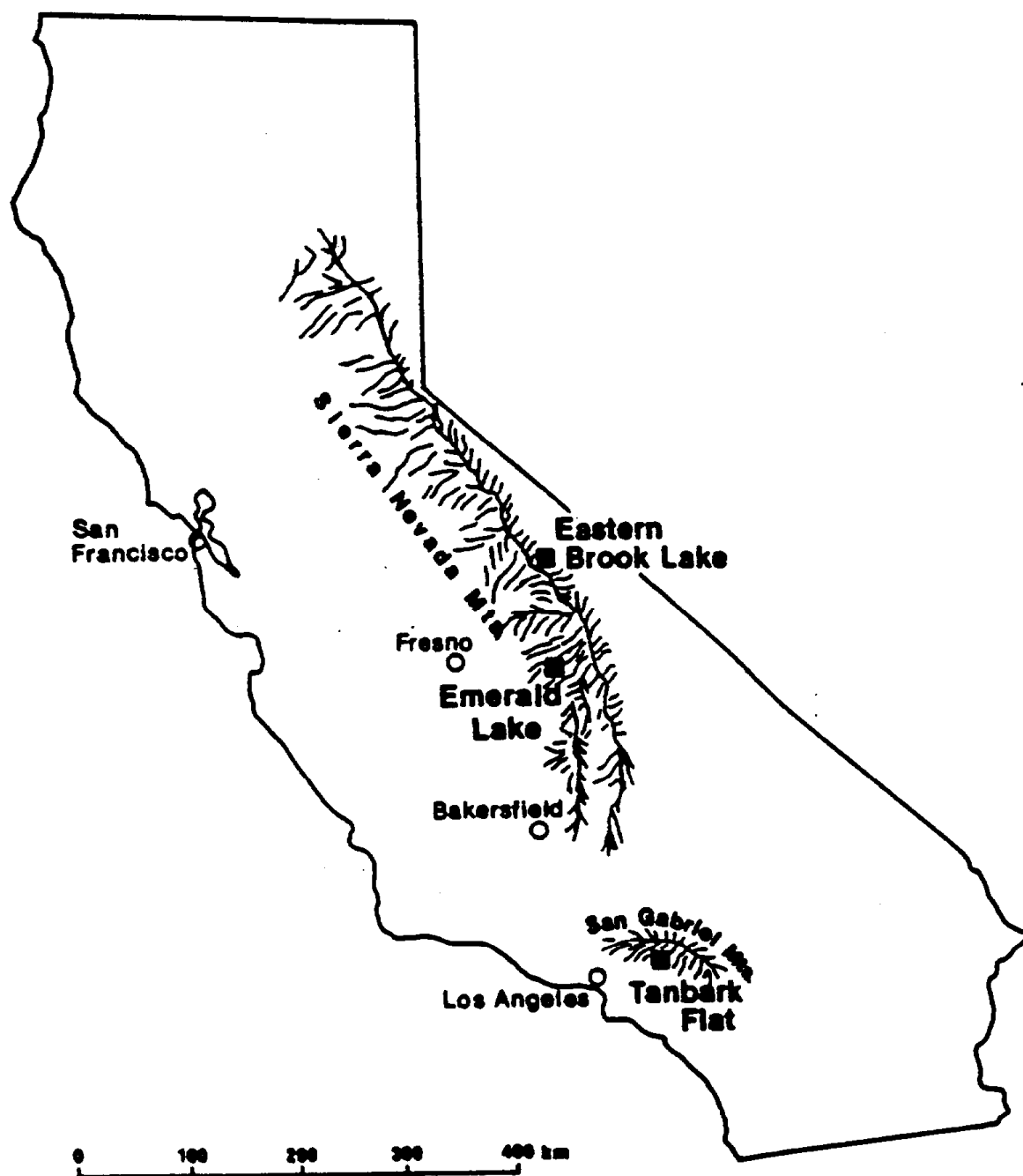


Figure 1. Location of the study sites in the mountains (black squares) and some major cities in California.

# PINUS CONCORDIA BRANCHES

(NO TEFLON)

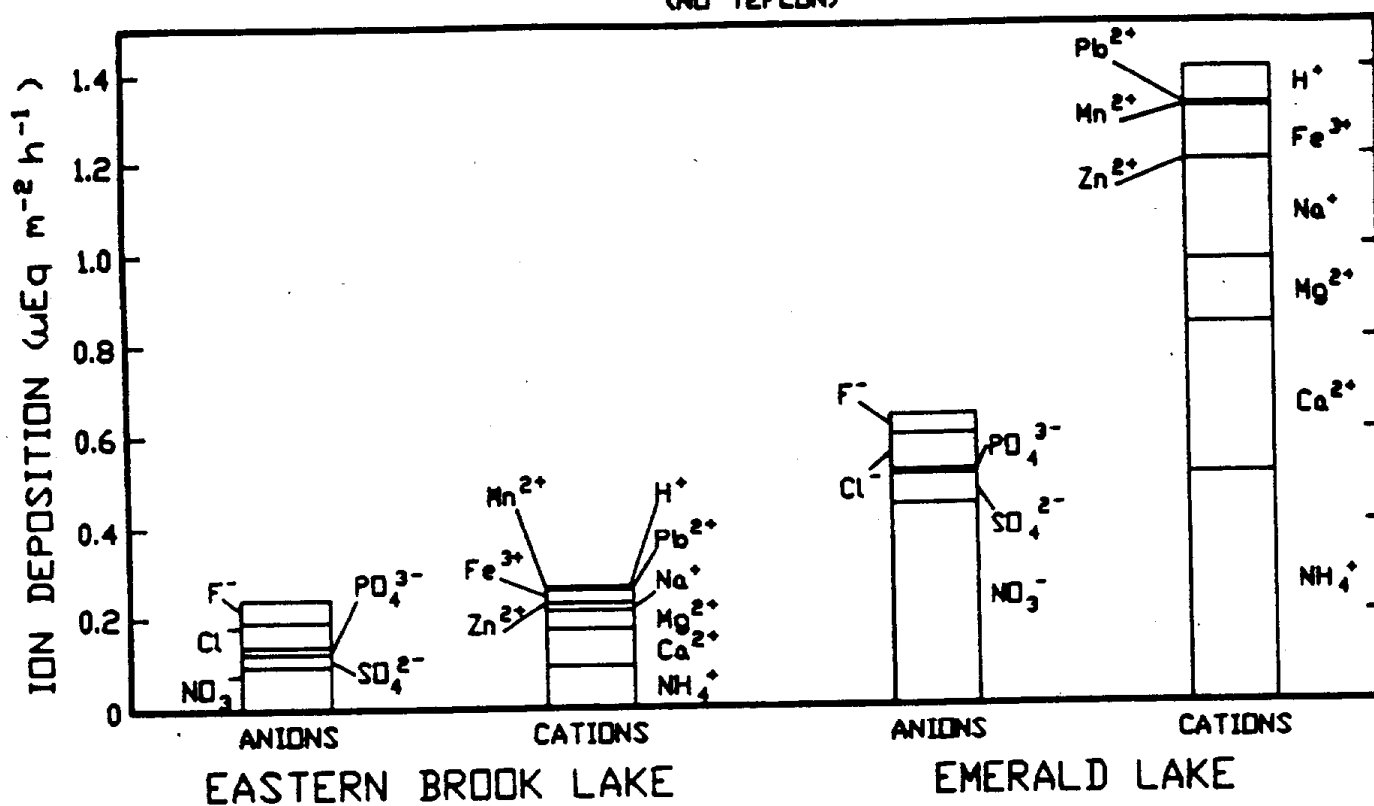


Figure 2. Deposition fluxes of ions to P. concordia at the Sierra Nevada sites - means for the entire study. For Eastern Brook Lake n = 6; for Emerald Lake n = 12.

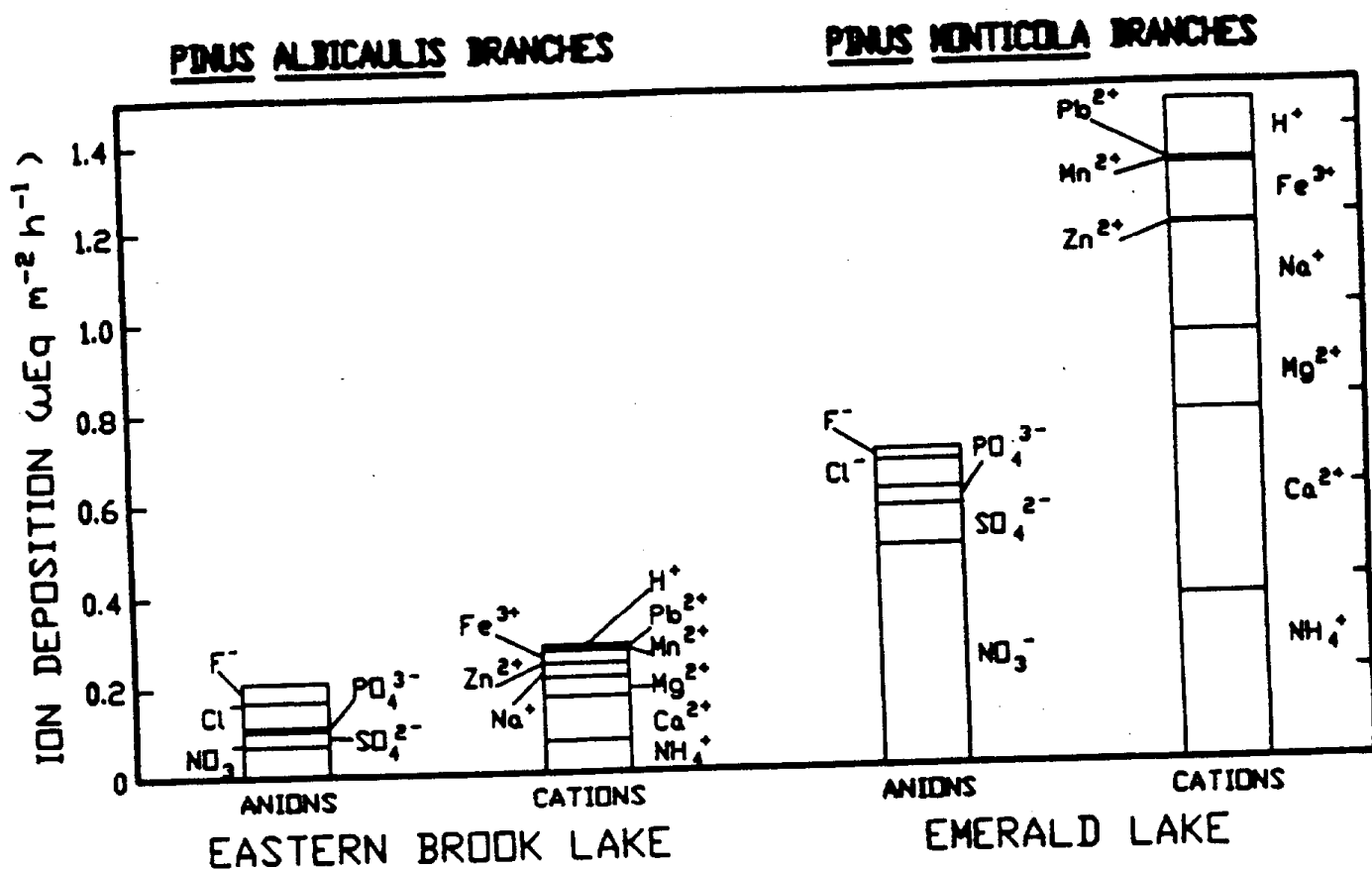


Figure 3. Deposition fluxes of ions to *P. albicaulis* (Eastern Brook Lake), and *P. monticola* (Emerald Lake) - means for the entire study. For Eastern Brook Lake  $n = 6$ ; for Emerald Lake  $n = 12$ .



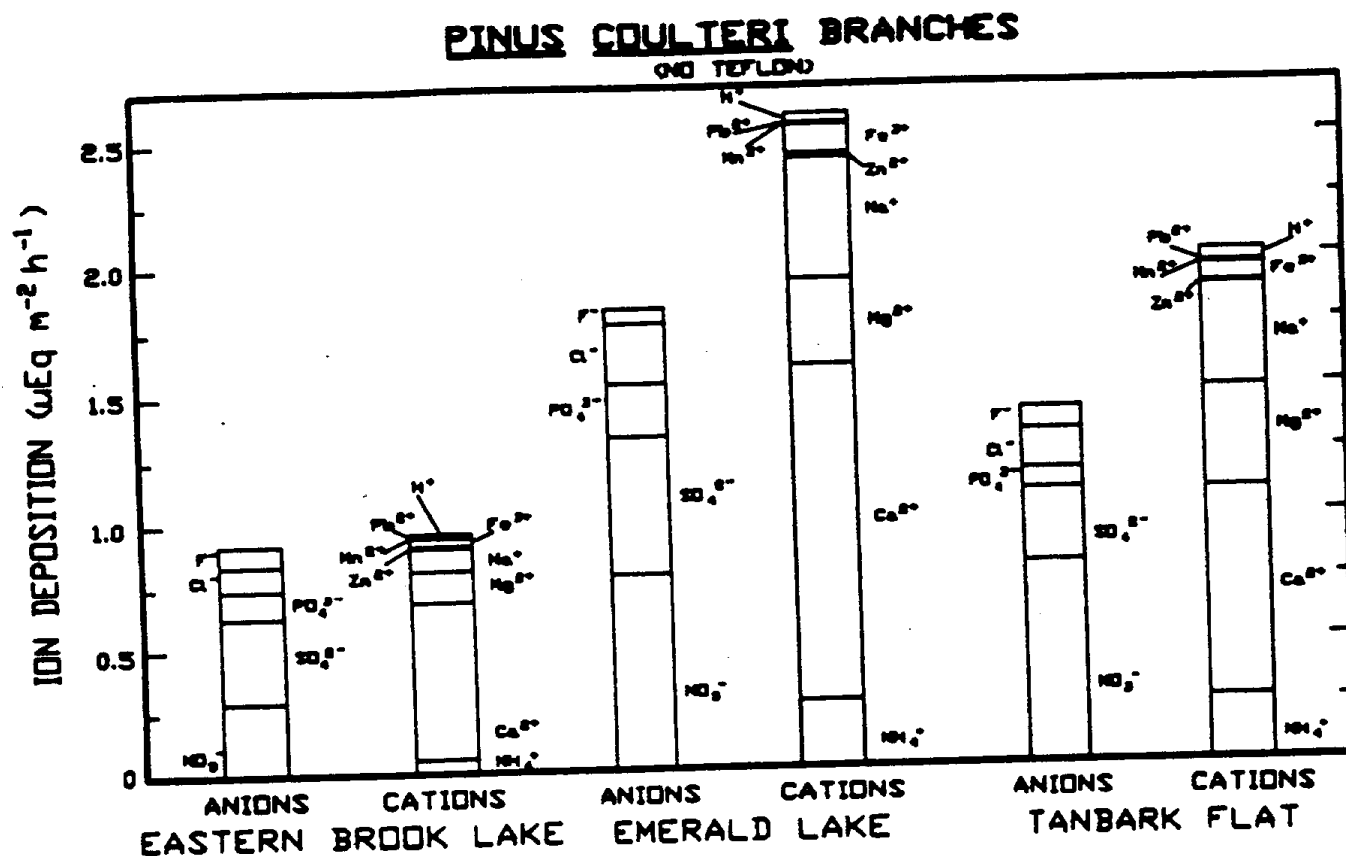


Figure 4. Deposition fluxes to potted *P. coulteri* seedlings at the Sierra Nevada and San Gabriel Mountains - means for the entire study. For Eastern Brook Lake and Tanbark Flat  $n = 8$ ; for Emerald Lake  $n = 12$ .

# PINUS COULTERI BRANCHES

ON TEFLON, CORRECTED FOR LEACHING

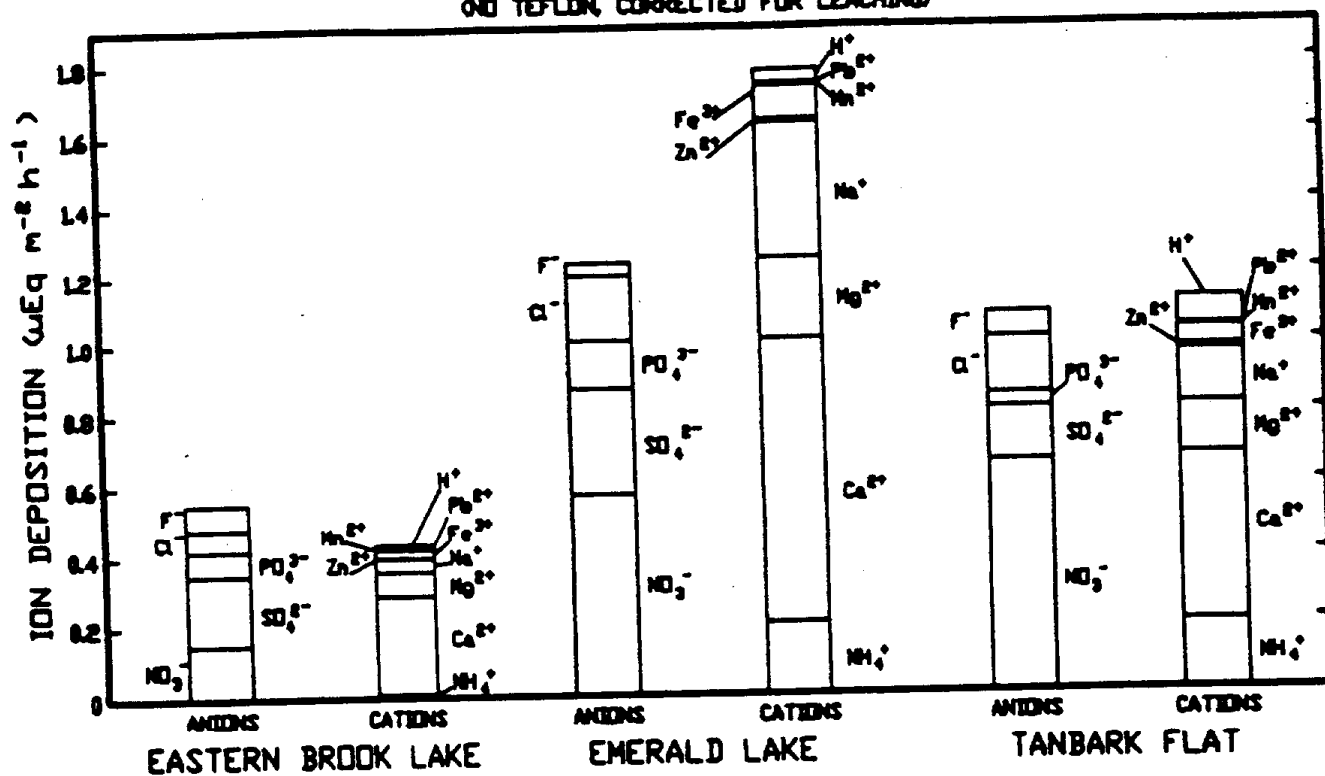


Figure 5. Deposition fluxes to potted *P. coulteri* seedlings at the Sierra Nevada and San Gabriel Mountains corrected for leaching during rinsing procedures (values from clean-air chamber subtracted) - means for the entire study. For Eastern Brook Lake and Tanbark Flat  $n = 8$ ; for Emerald Lake  $n = 12$ .

Table 1. Deposition fluxes of some ions to surrogate surfaces at three mountain locations ( $\mu\text{Eq m}^{-2} \text{h}^{-1}$ ) - means for pooled data for the entire study. For Eastern Brook Lake and Tanbark Flat  $n = 8$ ; for Emerald Lake  $n = 12$ .

Location	Nylon Filter			Paper Filter		
	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{H}^+$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{H}^+$
Eastern Brook Lake	0.300	0.012	0.225	0.531	0.126	0
Emerald Lake	0.579	0.069	2.057	0.696	0.157	0.131
Tanbark Flat	4.057	1.703	3.501	3.080	0.137	0.781

Table 2. Ratios of  $\text{NO}_3^-/\text{SO}_4^{2-}$  and  $\text{NH}_4^+/\text{SO}_4^{2-}$  (chemical equivalents) in dry deposition to foliage of native tree species at different United States locations.

Site	Tree species	$\frac{\text{NO}_3^-}{\text{SO}_4^{2-}}$	$\frac{\text{NH}_4^+}{\text{SO}_4^{2-}}$	Reference
Eastern Brook Lake, California	<u>Pinus concorta</u>	3.0	2.6	this work
	<u>P. albicaulis</u>	2.0	1.6	"
Emerald Lake, California	<u>P. concorta</u>	6.4	7.0	"
	<u>P. monticola</u>	5.0	3.8	"
Tanbark Flat, California	<u>Ceanethus</u> <u>crassifolius</u>	9.2	4.5	6
Warren, Michigan	<u>Quercus</u> sp.	2.1		14
Lapper County, Michigan	<u>Pinus</u> sp.	4.2	2.1	14
Walker Branch Watershed, Tennessee	<u>Quercus pinus</u> <u>Q. alba</u>	0.3	0.2	15

